
**THE REMOVAL OF HYDROGEN SULPHIDE
FROM GAS BY MEANS OF IRON OXIDE
WITH SPECIAL REFERENCE TO
HUMIDITY CONDITIONS**

BY

C. GORDON MILBOURNE

A

**DISSERTATION SUBMITTED
TO THE BOARD OF UNIVERSITY STUDIES OF
THE JOHNS HOPKINS UNIVERSITY IN CONFORMITY WITH
THE REQUIREMENTS FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY**

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THE REMOVAL OF HYDROGEN SULPHIDE FROM GAS BY MEANS OF IRON OXIDE WITH SPECIAL REFERENCE TO HUMIDITY CONDITIONS

INTRODUCTION

There is manufactured in the United States approximately 400 billion cubic feet of gas annually. For distribution as a public utility, hydrogen sulphide must be completely removed from this, and this may cost the industry, and ultimately the public, some five million dollars per year or more.

For this removal, the iron oxide process is at present chiefly used. When it is recalled that this is at present the most important process for the removal of hydrogen sulphide, not only in this country, but also throughout the world, it will be recognized that any study having as its immediate object the increase in the available knowledge concerning this process, with the ultimate purpose of increasing the efficiency and lowering the cost, is a subject of some general interest.

This general topic was therefore adopted as the subject of this dissertation. Since it was obviously impossible to develop the entire theme in the limits of such a study, a phase was chosen for intensive research. That water plays an important role in the reaction has long been recognized, as the subsequent historical discussion will show. Details covering the role and a knowledge of the control which should be imposed upon the water have, however, generally been lacking, or where available have been very imperfectly understood. This is largely due to the fact that the information has been developed with especial reference to the water content of the oxide. In commercial practice, however, it is extremely difficult or practically impossible to follow the water content directly. Accordingly, in this study major attention has been paid to the relative humidity of the gas,* and it will be shown that this is a factor of major importance in the commercial reactions between the iron oxide and hydrogen sulphide, and between sulphided iron oxide and air. Both reactions have been considered, and information concerning each is developed.

In this introduction, in common with general gas engineering practice, the term iron oxide has been applied to the ferric compound or compounds employed by the industry. A scientific examination of the material indicates that it may have a variety of compositions and

*Relative humidity is defined as $100p/P_s$, where p is the actual partial pressure of the water vapor and P_s is the vapor pressure of water at the same temperature.

structures. To deal with these effectively would prolong this study far beyond the limits available. The active agent appears to be a hydrated ferric oxide or ferric hydroxide. For simplicity, then, in accordance with practice, the term iron oxide will be applied to the purifying material, with the understanding that the author by no means considers the material to be simply ferric oxide. Where ferric oxide, or ferrous oxide are specifically meant, these scientific terms will be employed.

PART I—HISTORICAL

CHAPTER I

GENERAL DESCRIPTION OF IRON OXIDE PROCESS

The primary object of dry or oxide purification is to secure complete removal of hydrogen sulphide, H_2S , from the gas to be delivered for general public use, and the secondary object is to do this as economically as possible.

This removal of hydrogen sulphide takes place after the gas, which is manufactured in various units such as coal gas retorts or ovens, or coke ovens or water or oil gas generators, has been cooled in condensers and scrubbers, and the tar, which it may carry in suspension, has been extracted. After purification, the gas is metered and pumped into holders from which it is distributed for public use.

GENERAL DESCRIPTION OF PURIFIERS

The purifiers containing the oxide material are large flat boxes (M1, M2). These are usually arranged in series so that the gas passes through three or four in succession. These are so inter-connected that the order in which gas travels through them may be varied. That is, the gas may pass through in the order 1, 2, 3, 4 until it is necessary to replace the material in 1, after which the order is changed to 2, 3, 4, 1. The variations in order is usually continued until the box has passed through all four positions.

The purifying material in the boxes is supported on wooden grids. This material usually consists of a fluffing agent such as wood shavings on which the iron oxide is coated. Approximately 25 pounds of oxide is mixed with 1 bushel of shavings.

Method of Operation.—Approximately 0.5 square feet of cross-sectional area is required per 1,000 cubic feet of gas purified per day.*

The material through which this gas passes is used and converted to the iron oxide state for re-use until the accumulation of impurities in it renders its further use uneconomical. This conversion of the iron sul-

*This surface, of course, varies with the depth of oxide and concentration of the hydrogen sulphide in the gas. (See S13.)

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phide to the iron oxide is called revivification, and is brought about by the use of air, introduced either intermittently with the spent box out of service or continuously with it in service, or the material is removed for exposure to the air. This will be discussed and described later.

Raffloer Process.—A continuous process of dry purification has been developed by Raffloer (T2)* in which iron oxide or hydroxide or other suitable purifying material in finely divided form is blown into a desulphurizing chamber into which the gas is introduced and where the absorption of the hydrogen sulphide takes place.

Brady Process.—Another somewhat similar process is that of Brady of the U. G. I. Company of Philadelphia (U1). In one form, the apparatus consists essentially of two vertical concentric cylinders which are enclosed by a third. The oxide in finely divided form is introduced at the top and is allowed to gradually flow down through the annular space between the perforated walls of the inner cylinders and the spent oxide is removed at the bottom.

*The references will be found in the bibliography, page 82 ff.

CHAPTER II

OTHER METHODS OF HYDROGEN SULPHIDE REMOVAL

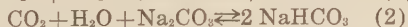
In recent years purification processes other than the dry iron oxide process have been developed in attempts to meet demands for methods which would be free of the inherent difficulties connected with this process, such as the large area required for purifying boxes. Reduction in the cost of installation and of operation have also been sought. These processes may be divided into two classes—Liquid and Catalytic.

LIQUID PURIFICATION

General.—In some of the liquid purification processes the investigators endeavored to imitate the process of dry purification by employing various iron compounds in solution or suspension. These are discussed by Sperr (S4), Jacobson (J2), and Ferbers (F6); the latter gives a very extensive résumé of liquid purification. Some, such as those described by Appleby and Lanyon (A3) and Sensich (S12), sought to make use of the ammonia recovered from the gas as in the Feld ammonia process. This is described by Terres and Overdick (T1) and by the British Patents (I1 and I2). According to Jacobson (J2), others proposed employing various metallic salts such as of iron and copper, various alkaline solutions, sulphur dioxide solutions, and sulphite solutions. Of all these, the three processes outlined below have been the most successful, and in a number of gas plants these have partially replaced the dry oxide process.

Sodium Carbonate or Seaboard Process.—The first of these processes to meet with extended commercial success in America was the Seaboard Liquid Process. A complete description of this process will be found in the articles by Sperr (S2, S4) and Cundall (C2). This process is based upon the scrubbing of the gas with a dilute solution of sodium carbonate, Na_2CO_3 . The apparatus for this consists essentially of two towers. In the first, designated the absorber, the gas meets a solution of sodium carbonate, which absorbs the hydrogen sulphide from the gas. In the second tower, named the actifier, the fouled solution from the first meets with an ascending large volume of air (air to gas ratio 1.25 for an inlet gas containing 330 grains of hydrogen sulphide per 100 cubic feet), and is regenerated by the reversal of the chemical reaction by which the hydrogen sulphide was absorbed. One or two dry oxide purification boxes are ordinarily used after the liquid purifier to remove the last trace of hydrogen sulphide from the gas.

The process involves the two reversible reactions:



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In the absorber these reactions proceed from left to right, while in the actifier conditions are made favorable for the reactions to proceed from right to left because the air removes the gaseous carbon dioxide and hydrogen sulphide.

This process possesses the disadvantage that the actifier air has a disagreeable odor. Therefore, although it is one of the cheapest and simplest methods for the removal of hydrogen sulphide and hydrogen cyanide, this has resulted in the development of other processes such as the iron and nickel sulphur recovery processes.

Sulphur Recovery Processes.—In the iron sulphur recovery process as described by Sperr (S1, S3) and Cundall (C1) the gas is brought in contact with a dilute solution of sodium carbonate in an absorber as in the Seaboard Process, but this solution also has an iron compound in suspension or solution. Furthermore, instead of an actifier, a "thionizer" is used for revivification of the purifying medium. In this so-called thionizer the solution from the absorber is subjected to the action of finely atomized air which revivifies the purifying medium, liberates free sulphur and separates this free sulphur from the bulk of any other solid material suspended in solution.

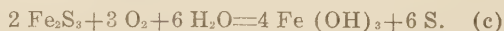
The primary reaction in the absorber is the same as in the Seaboard Process:



The sodium hydrosulphide, NaHS, reacts with the ferric hydroxide, Fe (OH)₃, in the presence of sodium bicarbonate as:



The oxidation of the ferric sulphide takes place in the thionizer with the regeneration of ferric hydroxide and the formation of elemental sulphur:



Besides eliminating the odor problem, this process recovers the sulphur from the gas.

A similar method is described by Cundall (C1, C3) in which nickel is used instead of iron. This is called the nickel or catalytic sulphur recovery process, and is based on the Seaboard Process, in which catalytic oxidation is used to free the sulphur of the sulphur compounds. Nickel sulphide in a "somewhat colloidal" form is the catalyst used in this process. It is prepared by adding nickel sulphate to the foul solution of sodium carbonate. It accelerates the reaction in the actifier where the liberation of free sulphur occurs according to the following reaction:



Other Methods of Hydrogen Sulphide Removal

CATALYTIC PURIFICATION

There are several plants in Germany purifying the gas from hydrogen sulphide by activated carbon and recovering the sulphur in solid form. A description of this process is given in a report in the Gas Journal (R1).

However, the catalytic purification processes have, in general, been developed primarily for the removal of organic sulphur with the removal of hydrogen sulphide as a secondary object. These are, therefore, only given brief mention here. A résumé will be found in a paper by Holtz and Huff (H1).

DISCUSSION

The comparative simplicity of the dry oxide process and the economic considerations relating to the replacement of present equipment are the basis for the belief that oxide purification will continue to hold a major place in the gas industry. Little change has been made in the iron oxide process since the use of this material for gas purification began about fifty years ago. However, in recent years it has been recognized that use of this material involves many problems much more complex than would appear at first.

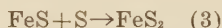
CHAPTER III

PREVAILING CONCEPTS OF THE REACTIONS BETWEEN IRON OXIDE AND HYDROGEN SULPHIDE

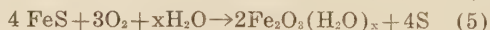
Perhaps relatively little progress has been made in the iron oxide process because, first, the reaction of hydrogen sulphide, H_2S , on hydrated iron oxides, $\text{Fe}_2\text{O}_3(\text{H}_2\text{O})_x$, is more complex than might be at first apparent, and, secondly, comparatively little study has been given to the reoxidation reaction. Pearson and Robinson (P1) give the first as the cause for the conflicting statements which are found in the literature concerning the course of the reaction and the products obtained.

Former workers found that the reaction of hydrogen sulphide on iron oxide gave a product which contained more sulphur than does ferric sulphide which has been obtained according to a simple double decomposition of these compounds.

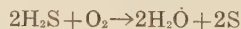
The prevailing concepts of the reaction which may occur in sulphiding under ordinary gas plant conditions are:



In reoxidizing the iron sulphide the following are among those accepted:



Summarizing the foregoing, iron oxide appears to act in the role of a catalyst for the reaction:



Reactions (1) and (4) appear to be the most important in gas purification.

Secondary reactions with hydrocyanic acid may occur when purifying coal gas. Offe (O1) gives the reaction for the formation of Prussian Blue, $\text{Fe}_4\text{Fe}_3(\text{CN})_{18}$, as



However, space permits only the mention of these to illustrate the complexity of the gas purification problem.

CHAPTER IV

PREVIOUS RESEARCHES ON THE REACTIONS BETWEEN IRON OXIDE AND HYDROGEN SULPHIDE

From a study of the literature, it appears that previous researches on the reactions between hydrogen sulphide and iron oxide have been complicated by the fact that the courses and rates of the reactions and the products obtained may be altered by changing the physical form or structure of the iron oxide used, or by changing the conditions under which the reaction is conducted.

FORMS OF IRON SULPHIDE

Gedel (G1) states that the literature records conflicting statements concerning the possible compounds containing iron and sulphur. Some of the sulphides of iron, according to Thorpe (T3), are: ferrous sulphide, FeS ; ferric sulphide, Fe_2S_3 ; and ferroso-ferric sulphide, FeSF_2S_3 . The sulphides which appear to be of the most interest in the purification of manufactured gas are: ferrous sulphide, FeS ; iron disulphide, FeS_2 ; and ferric sulphide, Fe_2S_3 . The last is perhaps the most important.

Gedel further states that the preparation of ferrous sulphide from its components by heating iron with sulphur demands a higher temperature than ever occurs in purification processes. In the latter, it is evident that the hydrogen sulphide must first reduce the ferric oxide to ferrous oxide, and that this can then further react with hydrogen sulphide to form ferrous sulphide. With regard to the iron disulphide, it should be noted that it can also be formed as a secondary product from the primarily formed ferrous sulphide and the separated free sulphur. In this, the heat liberated by the primary processes can play a part. For, "Iron disulphide is formed direct by heating ferrous sulphide and sulphur, or, with ferrous sulphide, from ferric oxide and hydrogen sulphide above 100°C ."

For a long time the existence of ferric sulphide, Fe_2S_3 , appears to have been doubted. Although its existence is admitted today, its chemical behavior is somewhat anomalous. According to Feigl and Bächer (F1), it sometimes reacts as if ferrous sulphide, FeS , were present, and the explanation advanced, namely, that this is due to the reducing power of hydrogen sulphide when an acid is added, is not altogether satisfactory.

PRODUCTS OF THE REACTION BETWEEN IRON OXIDE AND HYDROGEN SULPHIDE

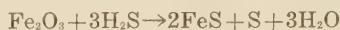
In view of the many forms taken by chemical combinations between iron and sulphur, it is not surprising that Gedel (G1) states, after a

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review of the work of previous investigators, that there are many conflicting statements regarding the exact nature of the product of the reaction between iron oxide and hydrogen sulphide. Some considered it to be a mixture of ferrous and ferric sulphide with free sulphur (Wright W1); others believed that ferric sulphide was at least part of the product. Berzelius (B2), Knapp (K4), Bolley (B3), D'Harcourt (H2), and Schilling (S5).

Gedel (G1) reported that in alkaline conditions the product was wholly ferric sulphide, while in acid conditions it was a mixture of mono- and di-sulphides (FeS and FeS_2) with free sulphur. Stone (S6) and Dunkley and Leitch (D2) support this view.

In opposition to this hypothesis regarding the formation of ferric sulphide is the other possibility, that in the purification process ferrous sulphide and free sulphur are formed, as would be represented by the reaction:



The supporters of this view include Wagner (W5), Schwartz (S7), and Allen (A1). These investigators found the product to be a mixture of ferrous sulphide and sulphur.

Offe (O1) gives the following formulae to represent the changes during the purification process:

- (1) $\text{Fe}_2\text{O}_3 + 3\text{H}_2\text{S} = 2\text{FeS} + \text{S} + 3\text{H}_2\text{O}$
- (2) $\text{FeO} + 2\text{H}_2\text{S} = 2\text{FeS} + 2\text{H}_2\text{O}$
- (3) $2\text{FeS} + \text{O}_2 = 2\text{FeO} + 2\text{S}$

When hydrogen sulphide reacts with ferric oxide the molar ratio of the iron to the sulphur in the product must always be as 2:3, whether as ferric sulphide, $1\text{Fe}_2\text{S}_3$; or as ferrous sulphide, 2FeS , and free sulphur; or as iron disulphide, FeS_2 , and ferrous sulphide. According to chemical theory, therefore, there must be 48 parts of sulphur to 80 parts of iron oxide. However, most workers agree in finding 2% more for sulphur than is theoretically possible, Deicke (D1), Rodt (R2), Brescius (B1), Cox (C5), Pearson and Robinson (P1), Wright (W1), Mecklenburg and Rodt (M3). Some attributed this to adsorbed air (B1), (M3) and (P1). Cox (C5) believed it was due to the decomposition of adsorbed hydrogen sulphide occurring during the subsequent analysis of the product. It seems probable, according to Pearson and Robinson (P1), that differences arise chiefly because the course of the reaction actually varies in different experiments, and the few analyses recorded have been insufficient to exhibit the variation fully or to establish an average course for the reaction. The difficulties involved are (1) the carrying the reaction to completion, (2) the complex nature of the product, and (3) the secondary reactions in, and possibly between, the substances primarily produced. They believed it probable that the course of the reaction varies within certain limits. However, they concluded that the primary

Researches on the Reactions Between Iron Oxide and Hydrogen Sulphide

reaction leads to the formation of ferric sulphide, and that some ferric sulphide decomposes with the formation of equimolecular proportions of disulphide and monosulphide.

These conclusions do not take into account the theory of Brescius (B1), who suggested the possible formation of free sulphur by the contact action of ferric oxide or ferric sulphide on hydrogen sulphide, which may decompose it into its components. This last explanation for the formation of excess sulphur could be verified by analysis of exit hydrogen sulphide for hydrogen formation during its passage over iron oxide. Moreover, the accuracy and applicability of the results of Pearson and Robinson (P1) to the conditions of practice are reduced by (1) the high temperature (100° C.) at which the experiments were conducted, (2) the caking of the material, and (3) the passage of dry air over the product in order to stabilize the weight before analysis. Cox (C5) found that even with the exclusion of air slight quantities of ferrous sulphate were formed.

From the results of Gedel (G1) the conclusion may be drawn that the action of hydrogen sulphide on the purifying material takes place according to the reaction:



From the above investigations, when ferric hydroxide and hydrogen sulphide react it may be assumed that ferric sulphide and sometimes ferrous sulphide and free sulphur are the primary products. Further, iron disulphide may be formed by a secondary reaction. This secondary course is especially unwelcome to the gas industry, for the iron disulphide formed is, as experiments show, not susceptible to revivification. The purifying material therefore becomes partially inert.

INVESTIGATIONS ON REVIVIFICATION OR OXIDATION OF PRODUCTS OF IRON OXIDE AND HYDROGEN SULPHIDE REACTION

Gedel (G1) studied the influence of air on the products of the fouling reactions and concluded that ferric sulphide and ferrous sulphide change completely to ferric oxide, with the precipitation of sulphur. He found, as indicated, that iron disulphide formed by the secondary reaction was not readily reoxidized. Furthermore, he states that in oxidation experiments ferrous sulphate was always formed, even if only in slight amount. Its formation was not influenced by moisture, but increased with increased temperature.

Because of these unrevivifiable products the purifying material in time becomes loaded with a constantly increasing mass which is useless for purification. As already pointed out in the last section, Gedel has further stated that the reaction actually does not go in this manner, but proceeds with the formation of ferric sulphide, which is converted into ferric oxide by oxidation with the separation of sulphur. He believes

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that a certain alkaline reaction is necessary for the formation of ferric sulphide. The formation of ferrous sulphate is dependent on the temperature and not on the moisture. Care must therefore be taken in revivification, by the use of proper depths and by supplying the proper moisture to the material, to keep the formation of ferrous sulphate at a minimum. Due to the presence of too much ferrous sulphate, a condition may occur which will facilitate the formation of ferrous sulphide, sulphur, and iron disulphide.

These last conclusions are supported by the data obtained by Stone (S6). Although all the results were not conclusive, he stated in his report that alkalinity increased the efficiency of many oxides, and that an alkalinity of about 2% (figured as CaCO_3) gave the best results. In his opinion the presence of lime had been of material benefit, not so much by increasing the total absorptive power as by increasing the activity or the rate at which the material removed hydrogen sulphide. In one of the plants operated by his company, the liming of the oxide with hydrated lime enabled the plant to remove completely the last trace of hydrogen sulphide, whereas, without lime, complete removal was impossible. Dunkley and Leitch (D2) obtained similar results. The addition of soda to a natural oxide (1 pound of commercial sal soda to 1 bushel of sponge, the latter containing about 25 pounds of the natural oxide) greatly increased its ability to remove the last traces of H_2S from water gas in a plant.

The oxidation of the product of the sulphiding reaction was observed by Pearson and Robinson (P1). They concluded that the product of the reaction tends to oxidize when exposed to air, but is not pyrophoric until it has been extracted with carbon disulphide, indicating that the particles are coated with a film of free sulphur which, by preventing actual contact with air, gives the material an apparent stability.

Wright (W1) found the dry reaction product very pyrophoric while it oxidizes more slowly if wet.

Offe (O1) states that in Germany, in the operation of purifiers without the use of fluffing agents, a fresh, highly reactive oxide must be mixed with spent oxide in the proportion of three to one. The reactivity is thus diminished, so that the oxide does not heat up too quickly and only a small amount of water is evaporated. Pressure increase through the box is reduced to a minimum. Furthermore, the cyanogen is almost quantitatively removed under these conditions. However, in this country, where fluffing material is more abundant and the spent oxide less salable, it is general practice to use some such material. The efficacy of this distribution was indicated by the work of the writer of this dissertation, as will be detailed in Part II, Chapter II. As the experimental matter to be presented later shows, the rate of the reaction between hydrogen sulphide and iron oxide depends to some extent on the amount of exposed surface to the gas per unit weight of oxide. This is in opposition to Offe's use of the oxide without fluffing material.

Researches on the Reactions Between Iron Oxide and Hydrogen Sulphide

REVIVIFICATION IN PLACE

Continuous Revivification in Place.—It is common practice to add a small quantity of air to the gas at the inlet of the purifier for the purpose of bringing about the continuous revivification of the iron oxide. This is called revivification in place. Theoretically, only 0.4% of air will be required for the continuous revivification of a gas containing 100 grains of hydrogen sulphide per 100 cubic feet. According to O. B. Evans (E1), "Common practice admits from .75% to 2%." Choller (C4) has pointed out that it is possible that revivification of iron oxide will not take place in the presence of hydrogen sulphide.

Offe (O1) has studied this further, and states that in order to effect revivification of the oxide in place in a perfectly satisfactory manner, on the basis of 0.5% oxygen in the purified gas, the amount of oxygen that must be present in the foul gas is obtained from the following formula (for hydrogen sulphide concentration of approximately 400 grains per

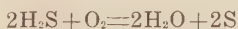
100 cubic feet). $0.5\% \text{ O}_2 + \frac{(\text{Volume } \% \text{ H}_2\text{S})}{2} \text{ O}_2$. The latter value of

oxygen disappears in revivification. Offe found that when the oxygen content is 0.3% by volume, no further activity of oxygen resulted.

The following table is taken from his publication:

	Oxygen, O ₂ % Vol.	Hydrogen Sulphide, H ₂ S	
		% Vol.	Grains per 100 cu. ft.
Gas entering purifiers...	0.7%	0.60% =	378
Gas leaving first box...	0.6%	0.14% =	88
Gas leaving second box...	0.5%	0.00%	0
Gas leaving third box...	0.4%	0.00%	0
Amounts removed			
in purifiers.....	0.3% O ₂	0. 6% H ₂ S =	378 gr./ 100 cu. ft.

Thus each 0.1% oxygen may remove approximately 125 grains of hydrogen sulphide per 100 cubic feet of gas purified. This was further studied by Seil, Heiligman and Clark (S8). These investigators state that "practice has shown that the oxygen content of the gas must be at least 0.4%, and that the active oxide must be 15% fouled," before advantage can be taken of the secondary catalytic reaction:



In their opinion, ferric sulphide is the catalyst for this reaction. They further state that each 0.1% oxygen above the "critical point" of 0.4% reacts with about 125 grains of hydrogen sulphide per 100 cubic feet of gas. Furthermore, there is no change in the oxygen content of the gas passing through the purifiers when the entering gas contains

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0.4% oxygen or less. However, when the oxygen content of the gas entering a purifier is above 0.4% the content will be reduced to this amount, unless the oxygen in the entering gas is in excess of the amount which can react with the hydrogen sulphide in the gas.

These investigators report that when a gas containing 400 grains of hydrogen sulphide per 100 cubic feet and 0.6% of oxygen passed through a partially fouled oxide, the oxygen reacted catalytically with 250 grains of hydrogen sulphide and left only 150 grains for the iron oxide to absorb.

While the catalytic nature of this reaction is questionable under ordinary gas plant conditions, the indication of a minimum oxygen concentration appears to be in accord with the results of Offe (O1) and was verified to some extent by the author of this dissertation.

Heats of Reaction.—In considering revivification in place, attention must be given to the heat generated by the sulphiding and revivifying reactions. If this heat becomes too great, the operation of the process is seriously impaired.

Fulweiler (E1) states that the total heat generated in the combined sulphiding and revivifying reactions when starting with ferric hydroxide is about 3,300 B.t.u. per pound of hydrogen sulphide removed. He further states: "Accurate values for the heat of formation of ferric sulphide seem to be lacking, but it appears that if ferric sulphide alone were formed, about one-third of the heat, or about 1,100 B.t.u. per pound of hydrogen sulphide, would be given off during fouling, and the remainder, or 2,200 B.t.u., would be given off in the revivification; whereas, if ferrous sulphide were formed, about 660 B.t.u. would be given off in the fouling and 2,640 B.t.u. in the revivification."

When purification and revivification are kept separate, the heat arising from the purification process is hardly perceptible, partly because of the great dilution of the hydrogen sulphide with the crude gas and partly because of the passage of the heat to the purifying material and to the metal walls of the purifier. But when purification and revivification occur temporarily and locally at the same time, attention must be given to the heat generated, which now appears of about tenfold value. Under these conditions the operation should be watched to see that the revivification does not take place too quickly, thus making the temperature rise too high, for an increase of temperature gives rise to a heavy evaporation of water from the hydrated iron oxide which dries out the mass. When the mass contains no more moisture, the temperature rise may become more rapid, sulphur generated by the revivification may melt, an agglomeration of the mass may be brought about, and the working of the purifier may thus be hampered.

Intermittent Revivification in Place.—Some operators prefer to use an intermittent method for revivification in order to eliminate the re-

duction in the calorific value of the gas by the continuous addition of small quantities of air used when continuous revivification is practiced.

Intermittent revivification in place consists in valving the purifier box to be revivified out of service while a large volume of air is blown through the oxide mass. Evans (E1), after a study of some twenty-five gas plants using revivification in place, stated that this method has been in successful use for a number of years in several plants. In others, however, this procedure has led to fires, and has accordingly been abandoned.

Possible Revivification With Steam at High Temperatures.—In one of these plants a box caught fire, and the attempt to extinguish it by circulating inert gases, consisting of carbon dioxide and nitrogen, failed because of the insufficient volume and velocity of these. However, upon the substitution of water gas for the inert gas at several times the previous rate, tests for hydrogen sulphide showed 2,000 grains per 100 cubic feet on the outlet of the box, whereas the inlet only contained a few grains. It is stated: "Subsequent experiments in the laboratory showed very clearly that hydrogen sulphide is formed at a temperature of 212° by the passage of steam over iron sulphide, and that its production increases rapidly with a rise of temperature." These results indicate the reversal of the sulphiding reaction when moisture is present in the gas. This effect was further studied by the writer of this dissertation, and while the results obtained at 100° F. were not conclusive, these also suggested the direct reoxidation of the iron sulphide by moisture. This moisture, in the absence of oxygen may be a cause of the reversion often noted. In this a gas clean on entering leaves a box holding sulphided material slightly foul. In the presence of oxygen, however, this probably would not occur, as will be indicated in Part II, Chapter III.

Revivification by Removal From Purifier.—Seil, Heiligman and Clark (S8) state: "The method of revivification usually depends on plant conditions. Where space is available, the authors favor revivification by removal from the box, allowing the fouled sponge to remain exposed to the air until the oxidation of the ferric sulphide is complete." The following quotation from the same article states the advantage to be obtained by this system: "In this way all lumps of sponge which have formed in the box during fouling are broken up before the sponge is replaced, and danger of channeling from this source is almost completely eliminated." Against this advantage is, of course, the labor cost for removing and recharging the oxide.

THE EFFECT OF MOISTURE—FERRIC HYDRATE

As stated above, the heat of the sulphiding and revivification reactions, particularly the latter, may become excessive and reduce the efficiency of the process. Another factor contributing very considerably to the decrease in the efficiency of operation of a purifier is the loss in water content of the hydrated iron oxide.

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Gedel (G1) states that the research of Brescius (B1) leads to the conclusion that dry hydrogen sulphide exerts no action on dry ferric oxide, and also that moist hydrogen sulphide acts on dry ferric oxide only slowly, and with small heat generation. These results were probably due to the manner in which the oxide was dried. Thus Weyman (W4) states that it has been generally considered that an oxide must be in the hydrate form in order to be active, probably because the strongly ignited oxide is very inactive when cold. However, his investigation showed that ferric hydrates dehydrated at as high a temperature as 650° C. continued to react with dry hydrogen sulphide when cold. Therefore, he concluded that the chemical activity of iron oxide is dependent primarily on the molecular structure, and not on any particular degree of hydration. He stated that the reactivity of ferric hydroxide toward hydrogen sulphide varies with the temperature (between 100° C. and 800 C.), at which the hydroxide has been dried, and that this variation may be explained in terms of the difference in molecular structure. He was of the opinion that the molecular structure was in most cases evidently derived from some form of hydrate.

After an exhaustive study Nicolardot (N1) has claimed to have established the existence of at least six modifications of ferric hydrate. These differ in their solubility in water and in other physical and chemical properties. Four of these forms are polymers of ferric hydrate.

In a research of Van Beimmelen and Klobbie (V1) it was shown that the water content of iron hydroxide is dependent (1) on the modification which it has suffered on drying, (2) on the tension of the water vapor, and (3) on the temperature. Weiser (W3) gives a thorough discussion on the various hydrated forms of iron.

Fulweiler and Kunberger (F4) have published a very interesting study of the physical characteristics of ferric oxide which includes a number of ultra-microscopic photographs.

A more recent research on the iron oxide-water system was conducted by Huttig and Garside (H3), who concluded: "That complete dehydration of ferric oxide with the conservation of its activity is as yet impossible."

Other recent researches on hydrated ferric oxide are those of Krause (K1, K2, K3), Shpitalskii (S9), Simon (S10), Albrecht (A2), Prakask (P2), Freundlich (F2), and Veil (V2). Albrecht gives some excellent X-ray photographs of several forms of hydrated iron oxide. The work of Krause on the peptisation of fused ferric oxide is of particular interest since it might, with further study, be applied to the reactivation of an oxide which has been overheated in a purifier box. This investigator also studied the transformation of the dark reddish brown "ortho-ferric hydrate" to the bright yellow "meta-ferric hydrate." A test conducted by the writer of this dissertation on this transformation, while not con-

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clusive, appeared to indicate that the yellow form was less active toward hydrogen sulphide than the reddish brown form.

Theoretically this would be expected, because, according to Krause, the fresh dark hydrate is much more finely divided than the yellow oxide, i. e., the particle size of the ortho-ferric oxide is much smaller than that of the meta-ferric oxide. Therefore, with this particular oxide the dark reddish brown form may be more reactive with hydrogen sulphide due to its offering more surface to and more intimate contact with the gas.

Dunkley and Leitch (D2) found:

"1. The activity of iron oxides for H_2S is effected by water content. Each oxide has a best water content or range of water content. Increasing or decreasing the water content beyond this range decreases activity.

"2. The activity of some oxides is confined to a very narrow range of water content, but the activity of other oxides may continue almost constant while their moisture content increases several hundred per cent.

"3. The activity of dark red or black oxides is usually more sensitive to changes in water content than is the activity of the yellow or yellowish-brown oxides. The latter oxides are usually of lower specific gravity and retain more moisture when apparently dry.

"4. An oxide that has been dried and then remoistened does not immediately regain the activity corresponding to its water content. Complete readsorption may require several days or weeks. If the oxide is dried at temperatures of $400^{\circ} C$. it readsorbs water even more slowly.

"5. A thoroughly hydrated oxide that has sulphided and then revived in the presence of plenty of water tends to resume the state of hydration which it had prior to sulphiding. A dehydrated oxide similarly treated tends to resume the dehydrated state even in the presence of excess water. From this it seems that throughout the sulphiding and revivifying process an oxide retains essentially the same physical structure."

Slack (S11) states that an oxide such as a natural Dutch bog ore may contain 60% moisture without appearing wet. However, it requires some time before evaporation brings the moisture content down to its optimum figure, and in some cases there is a time lag of days before the oxide becomes appreciably active, whereas with a British oxide, which appears wet, with a water content above 30%, becomes active at once at 28% water content. The temperature rise of the oxide box is much more rapid with the British oxide, probably being due in a large degree to less heat being used to evaporate the water content of the oxide. The influence of the varying water content of oxides while in use has perhaps been underestimated.

From the above observations, made in England, and also from the results obtained in this country by Cook (F3), with the use of steam in

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oxide boxes, it can be seen that a box may be getting too little or too much steam, i. e., the water content of the oxide may be either below or above the optimum point, respectively. This has been substantiated by the work of Dunkley, and Leitch (D2), and also by the writer of this dissertation, using an entirely different method of testing. In connection with the use of steam in purifier boxes, it has been suggested by Bagshaw (S11) that coils be used instead of allowing wet steam to go into the purifiers.

THE EFFECT OF TEMPERATURE

The factors classified by Slack (S11) as having important bearing on oxide purification are: (1) temperature which probably has the distinction of being first in importance, and (2) moisture content, which is dependent to a large extent on the temperature maintained in the boxes.

Stone (S6) states in his report that, although the study of the effect of temperature on oxide purifiers was very incomplete, the conclusions were drawn: "(1) Up to 110° F., as the temperature is increased, the per cent of hydrogen sulphide removed increases rapidly. (2) Above 110° F. care must be taken, as the velocity of the reaction becomes so great that the heat liberated may not be radiated away fast enough and the temperature will build up to such a degree as to result in the evolving of sulphur compounds."

Dunkley and Leitch (D2) also conclude that "The activity of oxides increases with increasing temperature to about 120° F.; above that temperature some oxides show only a slight decrease of activity, others show more. The total change in activity between 40° and 120° F. amounted to about 10%."

Seil, Heiligman and Clark (S8) believe that in general plant practice "it is preferable to keep the temperature between 85° F. and 110° F." While observations of the writer of this dissertation on this point were neither complete nor conclusive, evidence will be offered later which suggests that the optimum conveniently obtained plant temperature is about 95° F.

It is suggested from the above discussions that the existence of an optimum temperature for oxide purification may be due to the increase in the rate of reaction with an increase in the temperature, counter-balanced by a change in the structure of the iron hydrate-water system denominated iron oxide which may also be changed by increasing the temperature, and that these two effects give a curve which has its maximum at an optimum temperature. The matter should be investigated further with the aid of methods developed in this dissertation.

Gedel (G1), in discussing this change in structure, stated that the moisture content of freshly precipitated ferric hydroxide varied according to the temperature and the humidity of the atmosphere so that he

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never obtained a completely similar product twice. He also noted that ferric sulphide oxidizes more rapidly in moist than in dry air.

The determination of the proper moisture content of a hydrated oxide for the most efficient operation of gas purification and the maintenance of this optimum condition has been recognized as difficult. Stone (S6) gives the following reasons for this difficulty: "What would be a correct amount of moisture for one oxide might be an excess for another. Moreover, the proper amount will vary with conditions in the plants in which it is to be used." Among such varying conditions are (a) temperature, (b) saturation of gas with moisture as it enters boxes, and (c) hydrogen sulphide concentration. "Finally, whatever moisture was in the oxide at the start would remain constant but a short time, on account of the formation of water by the reaction of the oxide with H_2S and because the gas itself would either deposit or remove moisture, according to its temperature and degree of saturation."

Fieldner (F3) discussed this further and reached similar conclusions.

CHAPTER V

PROBLEM

A review of the above researches shows that for nearly fifty years it has been known that the water contained in the oxide itself has some effect in removing hydrogen sulphide from gas (D3). The addition of steam to the gas entering the purifiers has been practiced for some years in a number of plants. Moreover, it has become generally recognized that there is an optimum moisture content of the oxide if the best results are to be obtained. It has also been suggested by Fieldner and others (F3) that the water content of the gas stream has some effect on the maintenance of this optimum moisture content. However, it will be seen from the discussion in Chapter IV that former investigators seemed to place the emphasis on the water content of the oxide itself rather than on the relative humidity of the gas stream. Furthermore, it appears that no information has hitherto been available to indicate the correct humidity conditions for maintaining the optimum moisture content of the oxide. Moreover, no attempt, to the knowledge of the writer of this dissertation, has been made in previous investigations to differentiate between (a) the effect of humidity on the sulphiding reaction in which hydrogen sulphide is removed to form iron sulphide, and (b) the effect of humidity on the revivification reactions in which the iron sulphide and the oxygen of the air react to re-form iron hydrate. The researches of Gedel (G1) and Rodt (R2) appear to have been the only ones in which an increased rate of revivification of ferric sulphide with increased moisture content of the air was even noted.

PURPOSE OF RESEARCH

Therefore, as pointed out by Huff (H4), one of the major objectives of this research was the determination of the correct humidity conditions for maintaining the optimum moisture content of the iron oxide.

Another major objective was a somewhat general study of the revivification reaction. Compared to the researches already made upon the sulphiding reaction, there appears to have been very little work done upon revivification.

In the study of the humidity problem it was believed expedient to investigate the effect of the weight of oxide per unit surface, the hydrogen sulphide concentration, and the effect of rate of gas flow, as these more important secondary variables directly affect the particular method of investigation.

Problem

A major and final phase was the application of the laboratory results to plant practice. In the study of this, there were two primary objectives: first, the determination of the importance of humidity control in oxide purification, and second, the attainment of this control.

CHAPTER VI

DESCRIPTION OF PREVIOUSLY PUBLISHED TESTS

One of the very first of the necessary steps in the development was the adoption of a satisfactory method for testing the oxides under various conditions. A brief description of some of the more important present-day American tests and a discussion of some of their limitations is therefore given.

The best known of these tests are:

- (1) Fouling tests.
 - (a) Kunberger test (K6, G2, D4).
 - (b) Seil modification of Kunberger test (S8).
- (2) Experimental box method of Stone (S6, D4).
- (3) One-minute activity test of Dunkley (F3).
- (4) Rate of flow-activity tests.
 - (a) Fieldner, Powell and Scott test (F3).
 - (b) Dunkley and Leitch modification (D2).
 - (c) Jacobson modification (J1).

DEFINITIONS OF ACTIVITY AND CAPACITY

Before describing these tests, which seek to determine the usefulness of iron oxide for the purification of gas, however, it may be well to define the two properties which determine this usefulness.

These are activity and capacity.

Activity.—The *activity* may be defined as the rate at which an oxide causes hydrogen sulphide to be removed from a gas either in the absence of, or presence of, oxygen. Seil, Heiligman and Clark name the activity in the absence of oxygen the *theoretical activity*, and in the presence of oxygen the *actual activity*.

Capacity.—According to these same writers a distinction should be made between *theoretical capacity* and *actual capacity*. They state: "The *theoretical capacity* is the amount of hydrogen sulphide a gas purifying material removes from a gas containing H_2S in the absence of oxygen."

Description of Previously Published Tests

"The *actual capacity* is the amount of H_2S a gas purifying material removes from a gas under conditions similar to those obtained in practice, where the gas contains H_2S in low concentration in the presence of small amounts of oxygen," which partially revivifies the iron sulphide first formed.

Kohlmann (K5) states these briefly: "Activity is the rate of combining with capacity the ultimate amount of absorption of hydrogen sulphide."

(1) FOULING TESTS

(a) *Kunberger Test*.—In this method a five-gram sample of oxide is fouled by pure dry hydrogen sulphide for one hour. The water liberated by the reaction is retained in a tube containing calcium chloride. This tube and the tube containing the oxide are weighed together before and after fouling. As Dunkley and Barnes (D4) state, "the gain in weight of the two tubes is equal to the weight of hydrogen sulphide absorbed."

It will be seen that this test has to do with the capacity rather than with the activity of the oxide, and is thus a static test. It was therefore not applicable to the research described in this dissertation, because the problem here presented involved primarily a study of the kinetics of the hydrogen sulphide-iron oxide reaction.

(b) *Seil (S8) Modification of Kunberger Test*.—This test appears to be an improvement over the original Kunberger test, as it can give not only a measure of the theoretical capacity in one fouling, but also the actual capacity, and can therefore indicate the activity of an oxide. It also more closely approaches plant conditions in that it uses a gas containing about 400 grains of hydrogen sulphide per 100 cubic feet.

According to this procedure, manufactured gas is pumped through a bottle containing a solution of sodium bicarbonate and sodium sulphide, such as described by Jacobson (J1). These salts react to liberate hydrogen sulphide which is carried forward by the gas stream. As described by Seil (S8), the rate of gas flow is so adjusted that 36 grains of hydrogen sulphide per hour enter the first of a series of five tubes containing 120 grams of the purifying material as received, mixed with 60 grams of sawdust (screened 20-40 mesh), "and sufficient water, so the mixture contains between 45% and 50% moisture." The time required for a black stain to appear on lead acetate paper at the outlet of the first tube is taken as a measure of the "theoretical activity" of the material. The "theoretical capacity" is measured by the time which must elapse before the first tube ceases to remove any hydrogen sulphide from the gas. The fouled material is revivified and the test repeated any desired number of foulings. The percentage fouling is calculated after each test by determining the ratio of ferric oxide to hydrogen sulphide in a sample of the material under examination.

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The "actual activity" and "actual capacity" are determined by adding a few per cent of oxygen to the testing gas and making observations similar to those indicated above.

Seil (S8) states that curves may be drawn from the data obtained in this test for the comparison of different gas purifying materials, "under identical conditions, with respect to:

- "1. The lengths of time for which 100% efficiency is maintained.
- "2. The rate at which the efficiencies drop as the fouling continues.
- "3. Total amounts of H_2S removed."

The greatest disadvantage of this test appears to be the addition of water to the sawdust-oxide mixture in order to obtain a moisture content between 45% and 50%. This may or may not be the optimum condition for the particular oxide under examination. Therefore, this test may or may not give a fair indication of the maximum activity of an oxide. As Seil suggests, the effect of water could of course be studied. However, the time required for such a study appears to be excessive, since it usually required more than 24 hours to complete one test.

Another disadvantage is the difficulty of obtaining uniform distribution of the water in the oxide-sawdust mixture. Furthermore, it is difficult to obtain an even distribution of the oxide on the sawdust.

Still another disadvantage is the difficulty of packing the material in the testing tube in the same manner for each test.

(2) EXPERIMENTAL BOX METHOD OF STONE (S6, D4)

According to Dunkley and Barnes (D4, M2), "this method usually consists in fouling two oxides, one of known practical performance, the other the unknown material, with unpurified gas, in a pair of small purifiers. These purifiers may contain from a few quarts to a few bushels of the materials in one or more layers. "The purifiers are followed by gas meters to measure the gas passing through each oxide. The test usually consists in passing gas through both materials at the same rate and noting the volume of gas purified by each until the time some hydrogen sulphide passes one material, as shown by a test with lead acetate paper at the outlet." The rate of gas flow is generally twice that usual in practice.

As Kunberger (K5) states, this method requires too much time and attention to be of use as a laboratory test method.

(3) DUNKLEY (F3) ONE-MINUTE ACTIVITY TEST

This method depends upon the measurement of the activity by determining the amount of pure hydrogen sulphide gas which will be absorbed by a unit amount of iron oxide (1 gram) in a given time (1 minute)

Description of Previously Published Tests

“that is less than the time required for complete saturation of the active material.”

As the true measure of activity of an oxide is its ability to absorb hydrogen sulphide from a gas containing only a small percentage of this constituent and the above test uses pure hydrogen sulphide, this may not represent a true picture of the activity.

(4) RATE OF FLOW ACTIVITY TESTS

(a) *Fieldner, Powell and Scott (F3) Test.*—In this method the activity of a purifying oxide is determined by the maximum flow at which a gas containing a small percentage (200 grains per 100 cubic feet) of hydrogen sulphide can be passed through a tube containing a layer of the oxide (1 gram of oxide mixed with 0.5 grams of sawdust screened 20 mesh) to be tested without a trace of this constituent appearing at the outlet. Therefore, in this test, the more active the oxide the higher the rate of gas flow required in order that absorption may just fail to be complete.

The disadvantages of this method, as in the Seil test, appear to be difficulties which may be encountered in obtaining uniform distribution of the oxide on the sawdust and uniform packing of the material in the testing tube.

(b) *Dunkley and Leitch Modification of Rate of Flow Activity Test.*—This is an improved form of the last method, in which the conditions of testing are simplified. However, the same objections which were just noted appear to apply to this test also.

(c) *Jacobson Modification of Dunkley and Leitch Rate of Flow Activity Test.*—This is very similar to the one last described, but the method of hydrogen sulphide generation is greatly improved. This generation, original with Jacobson, is described in Part II, Chapter I.

REMARKS ON THE TESTS DESCRIBED

It will be seen from the descriptions of the above tests that in all these accurate control of varying humidity conditions would be particularly difficult. Further, the non-uniformity of oxide distribution on the sawdust, with its attendant non-uniform surface conditions, leave much to be desired. Moreover, the dissipation of the heat of reaction by the sawdust is probably not uniform.

PART II—EXPERIMENTAL

CHAPTER I

DEVELOPMENT OF TEST FOR STUDY OF IRON OXIDE HYDROGEN SULPHIDE REACTION

In order to permit a study of the interaction between iron oxide and hydrogen sulphide and the reoxidation of the iron sulphide thus formed, with particular reference to the effect of humidity conditions, the following tests were developed. These were designed to meet, or at least minimize, one or more of the seeming disadvantages or possible errors inherent in previous tests with respect to (1) the control of the humidity conditions, (2) the attainment of uniform surface conditions, and (3) the dissipation of the heat of reaction. A further advantage sought was speed, and this was attained, particularly in the sulphiding test. In the test developed, few determinations required more than three hours to complete. With routine testing, this time may be reduced to less than one hour. This compares favorably with that required for the rate of flow tests (F3, D2, D4, J1), and is much less than that required for the Seil (S8) and Stone (S6) methods.

Sulphiding Test.—The sulphiding test developed measures the comparative rate of fouling of iron oxide by hydrogen sulphide as shown by the color change. It permits the establishment and maintenance of various conditions of (1) relative humidity in the gas, (2) of the moisture content of the oxide, (3) of temperature, (4) of surface of the oxide, (5) of velocity of the gas stream, (6) of the concentration of hydrogen sulphide, and (7) of the constituents of the gas in a manner not, to the writer's knowledge, hitherto obtained. This comparative measure was secured by determining the time required for the color to change from the yellow or brownish red oxide to the black sulphide. This measurement was resolved into an empirical "hydrogen sulphide removal factor, C," which will be discussed later. The color change was noted as it moved along an expanse of oxide, over which the gas containing hydrogen sulphide was passed. The expanse was supported by a number of glass balls of uniform size coated evenly with a thin layer of the oxide undergoing the test.

The relative humidity was controlled by passing the gas through a humidifier containing a saturated salt solution. By using a dehydrating agent (phosphorus pentoxide) and by varying the salt* used, the relative humidity could be varied from 0% to 100%.

*Data on the relative humidities given by saturated salt solutions were obtained from the work of Leopold and Johnston (L1), Adams and Merz (A4), and the International Critical Tables (I3).

Test for Study of Iron Oxide-Hydrogen Sulphide Reaction

In order to remove constituents such as oxygen or sulphur compounds which might affect the reaction between the iron oxide and the hydrogen sulphide later picked up by the gas, the manufactured gas used was first passed over copper in a quartz tube placed in an electric furnace heated to 400° C.

The samples of oxide were brought approximately to the equilibrium moisture content by placing these for 18 weeks in desiccators containing the saturated solutions of the same salts that were used in the gas humidifiers. The desiccators were kept at a constant temperature (100.4° F.) in a cabinet thermostat.

Revivification Test.—In the revivification test, a number of the glass balls were coated with oxide to be tested, and these were then placed in each of the desiccators in the cabinet thermostat and the rate of revivification in the air at various humidities thus provided was noted. The time required for the color to change from the black sulphide to the brownish red oxide was recorded.

A general description of the apparatus and a detailed account of certain parts, together with details of the procedure, are given below.

GENERAL DESCRIPTION OF APPARATUS. FIGURE I.

The gas from the city supply was forced by the pump (22) through an electric furnace (21) containing copper turnings heated to 400° C. to remove any oxygen or sulphur which might be present. Bottle (19) served as a catch for the water formed, which would otherwise collect in the tubing and cause irregularities in the gas flow. The outlet tube was fitted with a three-way stopcock (18), one side of which was connected to the sulphiding bottle (16), while the other was directly connected to the humidifier (6), described later (see Figure 4). This gave an inert gas supply for purging the testing tube (T), which will be described later. The twenty-gallon sulphiding bottle (16) was three-fourths filled with a solution of sodium sulphide and sodium bicarbonate as suggested by Jacobson (J1). The desired concentration of hydrogen sulphide in the gas stream was obtained by varying the proportions and concentrations of the sodium salts. The following table gives the approximate concentrations of hydrogen sulphide in grains per 100 cubic feet obtained from fresh solutions at room temperature.*

Commercial		Approximate
NaHCO ₃	Na ₂ S	H ₂ S
grams per liter	grams per liter	grains per 100 cubic feet
20	16	120
63	42	300
Saturated	Approximately Saturated	650

*Increasing the temperature of the solution increased the hydrogen sulphide concentration of the gas.

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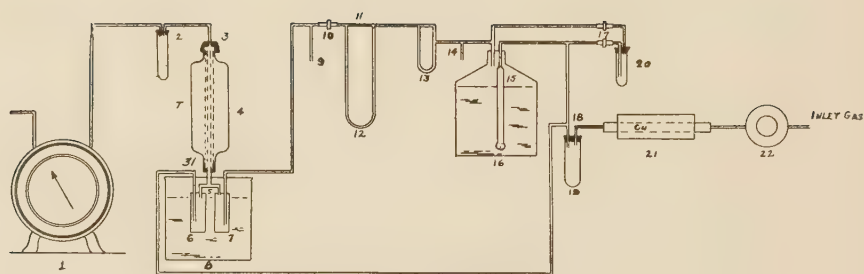


FIGURE 1—Diagrammatic Sketch of Apparatus.

Test for Study of Iron Oxide-Hydrogen Sulphide Reaction

The diameter of the inlet tube (15) of the sulphiding bottle was increased to 1.5 centimeters in order to reduce the tendency of sodium bicarbonate to deposit in this tube, sealing it off. A perforated bulb was blown on the bottom in order to introduce the gas into the solution in a stream of finely divided bubbles. Intimate contact between the gas and the solution is necessary at the higher rates of flow to obtain a constant concentration of hydrogen sulphide.

The gas containing the hydrogen sulphide then passed to a uniform flow regulator* (13) which was developed to maintain a constant gas rate for the extremely low rates of flow used in the tests (0.01 to 0.10 cu. ft. per hour). From the regulator the gas passed through an ordinary flow indicator (12). The capillary tube (11) for this was so chosen that a deflection of several inches of the water was obtained in the U-tube (12). The flow was varied by means of a screw clamp (10) on the rubber tubing connecting the indicator (12) with the humidifier (7) in the constant temperature bath (8) (described later, see Figure 2). A three-way stopcock (5)** was used to connect the humidifiers (6 and 7) to the pyrex testing tube (T), which was inserted in the rubber stopper (31) inside the jacket water bath (4) (described later, Figure 2). The tube (2) served as a catch for moisture, and was also used as a receiver for the lead acetate stain paper test. The glass tube (3) connecting this with the testing tube (T) was insulated with rubber tubing to prevent the condensation of moisture. The gas volume was measured at the outlet of the apparatus by a wet meter (1). Gas sampling connections were inserted at (9) and (14) for hydrogen sulphide tests, (14) was used only for snap samples and (9) was placed after the flow meter in order to obtain a representative gas sample. This arrangement was devised for the by-pass method used in the tests for studying the effect of changes in the hydrogen sulphide concentration. This involved by-passing a part of the gas around the hydrogen sulphide bottle (16). The amount so by-passed was regulated by screw clamps (17) and the bubbling bottle (20). The number of bubbles per unit time were counted with the aid of a stop-watch.

DETAILED DESCRIPTION OF SPECIAL APPARATUS

Oxide Testing Tube.—The oxide testing tube (T, see Figure 2) was an ordinary pyrex glass tube initially of uniform bore, one end of which had been drawn down to 3 mm. outside diameter, where it was inserted into the rubber stopper (31) at the bottom of the jacket (4). The tube chosen had an inside diameter only slightly greater than the glass balls to prevent excess by-passing of the gas around these balls (30), which were coated with the iron oxide. In the tests, 6.5 mm. inside diameter tubing was used with 6 mm. balls. Care must be taken that the tube is not of too small a diameter and that the interior is of uniform cross section throughout, otherwise the balls will stick in the tube. It was

*Described later, see Figure 3.

**Described later, see Figure 4.

Test for Study of Iron Oxide-Hydrogen Sulphide Reaction

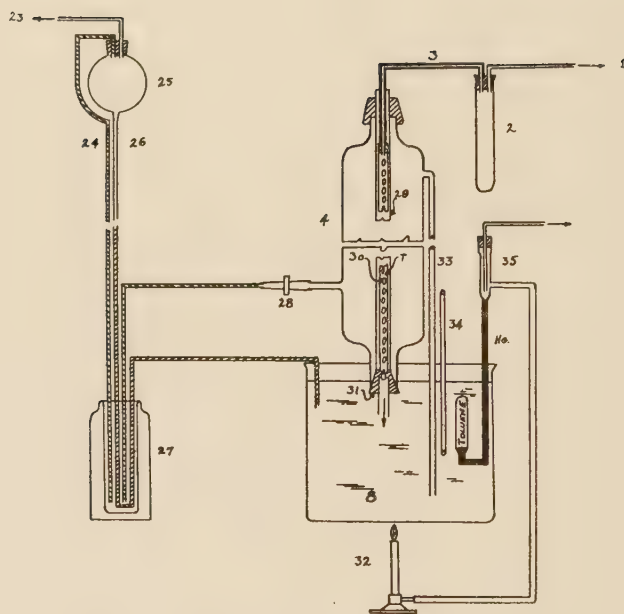


FIGURE 2—Oxide Testing Tube and Temperature Control.

Test for Study of Iron Oxide-Hydrogen Sulphide Reaction

indented at four diametrically opposite points near the bottom to prevent the balls from adhering in the tapered part below these indentations. The top was slightly flared in order that the connecting tube (3) might be easily inserted and the oxide covered balls easily poured into it. The length was 28 cm. and was limited by the space available for weighing in the cabinet of an ordinary analytical balance.

Constant Temperature Water Bath and Jacket.—The jacket (4, shown in Figure 2) was an ordinary Liebig condenser. It was maintained at a constant temperature by circulating water from bath (8) through it. This circulation was accomplished by the syphoning action of the tube (28). In effect, the jacket (4) and the tube (28) acted as the outlet leg of the syphon, and tube (33) served as the inlet leg. The rate of flow of the water through the jacket was regulated by a screw clamp on the outlet (28). The water was syphoned into the thermos bottle (27), from which it was pumped back into the constant temperature bath (8). An air lift operated by an ordinary suction pump was used for this purpose. The water in the bottom of the thermos bottle was trapped in the tube (24) in the form of drops by bubbles of air, and the whole was drawn up into the separator (25). The air was drawn out through the suction tube (23) and the water ran down tube (26) by gravity into the bath, thus completing the cycle. The tube (24) was chosen of larger diameter than (26) (10 mm. and 7 mm., respectively), thus preventing excess head of water in (24), as this would cause breaking of the water seal in the U-tube (26). The air lift would cease to function when this was broken. The tube (26) was therefore designed to take care of the fluctuations in the suction head. The temperature of the bath (8) was controlled by an ordinary mercury-toluene gas regulator (35) attached to the Bunsen burner (32). The temperature is measured by the thermometer (34) suspended in the bath.

Uniform Flow Regulator.—The operation of the regulator (13), which is shown in Figure 3, depended upon the drop in pressure across a constriction. This constriction may either be adjustable, as shown above, where it consisted of a screw clamp and rubber tubing, or it may be fixed by substituting a very fine capillary glass tube at (37). The position of the float valve was so adjusted that under ordinary conditions it was partially seated. This adjustment was accomplished by varying the position of the rubber tubing valve seat (39) on the glass tube (38). As the inlet pressure increased, thus increasing the flow through the orifice, the increase in pressure was transmitted from the inlet tube (36) by means of the mercury in the U-tube to the float valve (40). This caused the valve to seat itself more firmly, thereby reducing the flow. It may therefore be considered an automatically adjusting throttle which, as the pressure increased or decreased, increased or decreased the resistance to the flow of gas through the regulator. It was necessary to so adjust the valve seat that the valve could not adhere to it. This was accomplished by causing the tube (38)

The Removal of Hydrogen Sulphide From Gas

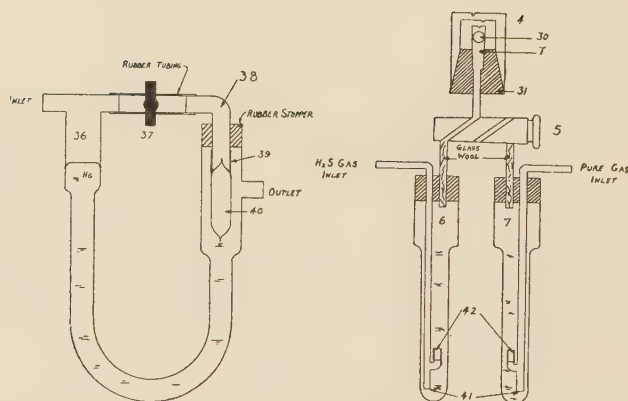


FIGURE 3—Uniform Flow Regulator.

FIGURE 4—Humidifiers.

Test for Study of Iron Oxide-Hydrogen Sulphide Reaction

to act as a stop so that when the pressure built up in the inlet (36) it could not force the float up into the tubing (39) beyond a certain point. All parts of the regulator were made of glass except those otherwise indicated.

Tests of this regulator were made over a period of several hours. No adjustments of the gas flow were made between readings. With a flow of 0.02 cubic feet per hour the variation was 0.0015 cubic feet, or about 7%. This variation could, of course, have been reduced had this been desired by placing another regulator in series, but this was not deemed necessary.

Tests of Uniform Flow Regulator.—

TEST NO. 1

	Time	Meter Reading	Time	Meter Reading
Finish	4:05	0.0567	5:06	0.0768
Start	3:22	0.0415	4:05	0.0567
Elapsed Time in Minutes..	43		61	
Cu. Ft.		0.0152		0.0201
Cu. Ft./hr....		0.0212		0.0198
Variation		.0014 cu. ft.=6.6%		

TEST NO. 2

	Time	Meter Reading	Time	Meter Reading
Finish			7:26	0.1277
Start			5:06	0.0768
Elapsed Time in Minutes..			140	
Cu. Ft.				0.0509
Cu. Ft./hr....		0.0198		0.0219
Variation		0.0021 cu. ft.=9.6%		

TEST NO. 3

	Time	Meter Reading	Time	Meter Reading
Finish			9:38	0.1785
Start			7:26	0.1277
Elapsed Time in Minutes..			132	
Cu. Ft.				0.0508
Cu. Ft./hr....		0.0219		0.0232
Variation		0.0013=5.6%		

*Humidifiers.**—The gas containing hydrogen sulphide was brought to an approximately known humidity by passing it through saturated solu-

*See Figure 4, page 32.

The Removal of Hydrogen Sulphide From Gas

tions of various salts. The bubbler tube caused intimate contact and produced a stirring effect between the solution and the gas by drawing a drop of the solution up through (41) and out at (42) with a bubble of gas. The low gas rate allowed time for approximating equilibrium conditions between gas and solution. Glass wool was inserted into the arms of the stopcock (5) to prevent entrained moisture from being carried up into the testing tube (T). The humidifying tubes (6 and 7) were enlarged at the top to assist in preventing entrainment.

Constant Temperature Cabinet.—The cabinet shown in Figure 5 was made from an ordinary refrigerator from which the partitions had been removed. The temperature was maintained by an electrical heater (45) placed in a 7-inch galvanized sheet-iron pipe through which the air in the cabinet was circulated by a 6-inch fan (43).^{*} A Wood's metal fuse (44) was placed in the heater circuit inside the cabinet to eliminate the danger of fire in case either the thermostat (50) or the relay (46) should fail to operate. The thermo-regulator was made of 1 centimeter thin wall pyrex tubing filled with mercury. The expansion and contraction of the mercury made and broke the relay circuit at a point in the capillary tube (49).

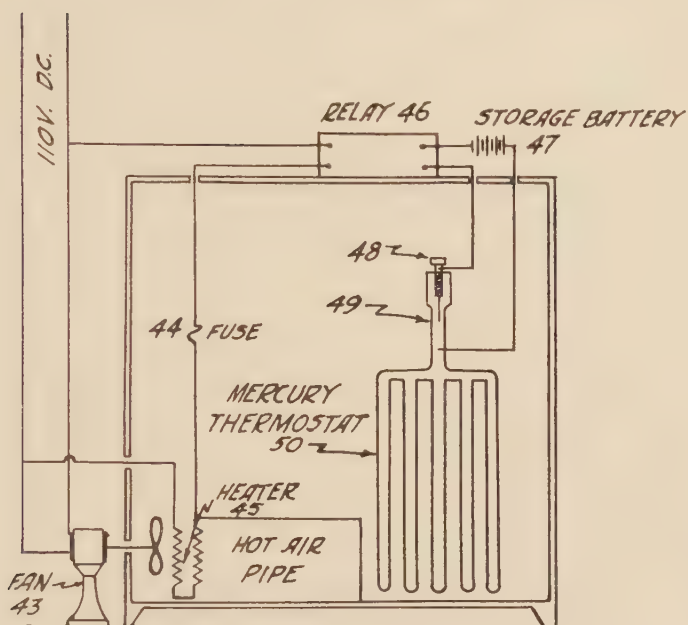
Adjustment of the temperature setting was made by means of the thumb screw (48). The temperature was maintained constant by varying the resistance in the heater circuit. The relay increased or decreased this by throwing a 25-watt electric bulb (51) either in series or in parallel with the heater. The detailed wiring diagram is shown in Figure 6. The two sources of power to the relay minimized the possibility of failure in its operation. The battery was placed on a trickle charge through the resistance bulb (53). Had either of these bulbs burnt out, thus breaking the power circuit, the battery would have taken up the load. The temperature was maintained within $\pm .2^{\circ}$ C., with the fan operating, and $\pm 1^{\circ}$ C. with the fan removed. The fan was used during the time in which the tests were made.

DETAILS OF METHOD OF TESTING

The testing was conducted as follows: About one gram of iron oxide, previously brought to equilibrium with one of the various humid atmospheres by long exposure in one of the desiccators, was placed in a 250 cc. Erlenmeyer flask with about 35 glass balls (30) of uniform size (6 mm. in diameter). A very thin and uniform coating of the oxide was obtained on the balls by whirling the flask in such a manner as to cause the balls to be vigorously rolled about. Precautions were taken to avoid moisture change during coating by bringing and maintaining the uncoated balls, flask and the atmosphere within the flask to the desired temperature and humidity in advance of the introduction of the oxide, as will be described in the first section of the next chapter. The balls were then placed in

^{*}The fan was placed inside the cabinet, however the motor could be placed outside to facilitate oiling.

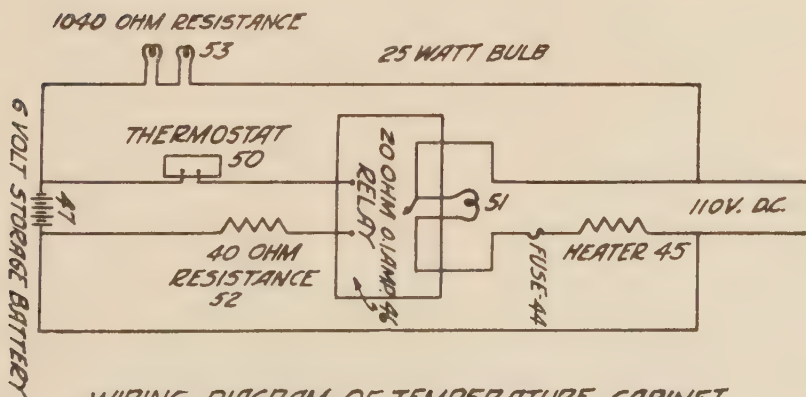
The Removal of Hydrogen Sulphide From Gas



CONSTANT TEMPERATURE CABINET
FIGURE 5

FIGURE 5—Constant Temperature Cabinet.

FIGURE 6—Detailed Wiring Diagram for Cabinet.



WIRING DIAGRAM OF TEMPERATURE CABINET
FIGURE 6

The Removal of Hydrogen Sulphide From Gas

the testing tube (T, Figure 2) and the whole was accurately weighed on an analytical balance. The weight of the tube (T) and balls (30) being known, the weight of the oxide was thus obtained. The testing tube was connected to the apparatus described above as follows (see Figures 1 and 2): First the testing tube (T) was attached to the connecting tube (3), the rubber tube insulation of the latter serving as a stopper. This assembly was then attached to the humidifiers (6 and 7) by placing the tube (T) in the constant temperature jacket (4) and pressing the tapered end into the hole in the stopper (31) at the bottom.

The apparatus was then swept out with humidified city gas, from which all traces of oxygen and hydrogen sulphide had been removed. The three-way stopcock (5) was then reversed so that the hydrogen sulphide containing gas passed over the oxide. A stop-watch was started immediately after this cock was turned and the rate at which the sulphiding proceeded was observed. This was done by noting the distance along the tube that the black color moved and the time required for this color change. The distance was measured by means of a special rule, which consisted of a strip of sheet brass 1 cm. wide and about 50 cm. long on which co-ordinate paper was pasted for graduation. This was inserted between the testing tube (T) and the inner wall of the jacket (4) in such a manner that both the balls and the graduations on the rule could easily be seen through the water jacket. Before each test the rule was adjusted in such a manner that the bottom of the first oxide coated wall was opposite the zero mark on the scale. The other readings necessary are shown below in the results of a typical test.

Results of a Typical Test.—Date, May 7, 1928. Temperature, 38° C. Relative humidity, 74.9%.

	Grams
Weight of tube+balls+oxide	56.6229
Weight of tube+balls	56.5842
Weight of oxide on column of balls 13.4 cm. in length..	0.0387
Average weight of oxide per unit length (cm.) of oxide column:	
Wet	0.00289
Dry	0.00189

Note—Owing to the shape of the supporting surfaces, the amount of oxide per unit length was not, of course, uniform. However, readings were made just as a ball had changed color. Thus, by observing homologous points on the column, comparable readings reduced to a unit length were permissible. Since balls of the same size were used throughout, this involved no error.

Test for Study of Iron Oxide-Hydrogen Sulphide Reaction

Tutwiler readings:

Beginning 9.1—5.5=3.6 cc. iodine solution equivalent to 360 grains per
100 cubic feet (8.23 grams per cubic meter)

End 9.4—5.8=3.6 cc.

Water content of oxide determined by ignition=34.5 per cent.

Distance (D) the black coloration traveled along tube in cm.:

	1.9	2.9	5.1	6.4	7.1	7.9	9.8
Time, in elapsed							
minutes . . .	2:35	5:00	10:20	12:45	15:00	17:45	21:30
$\log T$							
$K = \frac{\log T}{\log D}$	1.48	1.51	1.44	1.37	1.38	1.39	1.34
D	10.9		12.0		13.0		
Time	24:45		27:45		30:15		
K	1.34		1.34		1.33		
Average value of constant $K=1.391$							

$$\text{Hydrogen sulphide factor, } C = \frac{K}{\text{Av. wt. per unit length of column, dry basis}} = \frac{1.391}{0.00189} = 736$$

Wet-meter reading: 0.3740 at 32 minutes
0.3541 at 7 minutes

0.0199 cubic feet of gas passed in 25 minutes or 0.048 cubic feet (13.6 liters) per hour

Flowmeter: 0.85+0.68=1.53 inches (38.9 mm.) H_2O

Constants—The use of the constant K was adopted after noting that plotting on log-log co-ordinate paper the distance D against the time T gave an approximately straight line. It will be noted that in the example given the value of K rose to a maximum, then fell off, although the differences were not great. The empirical hydrogen sulphide removal constant, C , was adopted to permit the comparison of constants obtained in different tests.

CHAPTER II

RESULTS OF LABORATORY EXPERIMENTS ON SULPHIDING REACTION

In order to make a comparative study of the effect of various humidities on the sulphiding reaction, it was necessary to make a preliminary study of the effect of variations in factors other than the humidity which may affect the results of the humidity tests. It was primarily for this purpose that the tests on the effect of variations in (a) the weight per unit surface, (b) the rate of gas flow, and (c) the hydrogen sulphide concentration were made. In all tests the temperature was maintained constant at 38° C. (100.4° F.), as described in Chapter I. In order to eliminate the variable effects of possible impurities and heterogeneities of commercial oxides on the activity and capacity, it was necessary to prepare a chemically pure oxide for these studies.

METHOD OF PREPARATION OF TEST OXIDE

The chemically pure test oxide "G" was prepared from ferric nitrate, $\text{Fe}_2(\text{NO}_3)_6 \cdot 9\text{H}_2\text{O}$, Baker's Analyzed, Cl. . . . 0.001%, free HNO_3 present. Ammonium hydroxide was added to a cold solution of the nitrate until it was slightly alkaline to litmus. The precipitate thus formed was washed by decantation until the supernatant liquor upon test showed only a trace of nitrate. The concentrated sulphuric acid, ferrous sulphate brown ring test (Fresenius F5) was used. The hydrate was then washed on a Buchner funnel until there was no perceptible trace of nitrate present in the filtrate.

The oxide used for most of the tests made in the study of the effect of the variations in (1) the weight of oxide per unit surface, (2) the rate of gas flow, and (3) the hydrogen sulphide concentration, was prepared from "G" by air drying 100 hours at room temperature and was denoted as "GA." Analysis showed 34.5% water in the oxide at the time the tests were made on the effect of the variations in the weight of oxide per unit surface. After storage in a glass-stoppered bottle one year, the water content decreased to 28%, at which time the rate and concentration tests were made.

In the tests on the effect of humidity, the samples of oxide were brought approximately to equilibrium at the various humidities by spreading these in thin layers on watch glasses in the desiccators for 18 weeks at 38° C. In order to reduce to a minimum any change in the water content of the oxide between the time of removal of the sample from the desiccators and the starting of a test, special precautions were

Results of Laboratory Experiments on Sulphiding Reaction

taken. The Erlenmeyer flask containing the glass balls was placed in the cabinet and brought to 38° C. and the particular humidity under test, by passing air through the saturated solution required. The sample was then added and the flask stoppered, covered with a towel *** and shaken to coat the balls. This was done outside the thermostat. To evaporate any moisture which might have condensed in this process at the higher humidities, the flask was again placed in the cabinet. The balls were then quickly poured into the testing tube and weighed. Before starting a test the tube was purged with inert gas of the required humidity as described in the procedure.

THE EFFECT OF CHANGES IN VARIABLES OTHER THAN HUMIDITY

The Effect of Changes in the Weight of Oxide per Unit Surface.—The effect of variations in the weight of oxide per unit surface ** on the results obtained with the glass ball test developed for this research was studied primarily for the purpose of correcting the results of subsequent tests. In this study the humidity,* gas flow, temperature, and hydrogen sulphide concentration were maintained constant. It is shown in Curve I, which was plotted from data recorded in Table I, that the hydrogen sulphide removal factor, C (calculated as indicated in example shown in Chapter I), diminishes as the weight of oxide per unit surface increases. This may be due to the increased average thickness and consequent increased average resistance of the oxide film through which the hydrogen sulphide must penetrate after it has saturated the exposed outer layer.

Variations of K With Weight.—As previously stated, the hydrogen sulphide removal factor, C, for each test was calculated from the average value of K obtained for that particular test. It appears from the tests in which the weight per unit surface was varied that the logarithm of "K" is directly proportional to the weight of oxide per unit surface, i. e., the logarithm of K increases directly as the weight of oxide per centimeter of balls increases. This is shown by Curve 2, from which it follows that, within the limits of the tests,

$$\log K = FW + A$$

Where K=logarithm of time, T, divided by logarithm of distance, D.

F=constant proportionally factor for a particular oxide.

W=weight of oxide per unit surface.

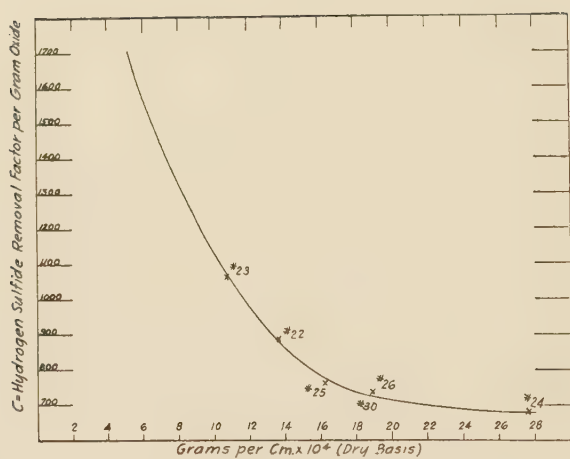
A=constant.

**The weight of oxide per unit surface is defined in this research as the weight coated on a column of uniform (6 mm. dia.) glass balls one centimeter long.

*The relative humidity was maintained constant at 74.9% in all these tests by passing the gas through a saturated solution of sodium chloride at 38°C.

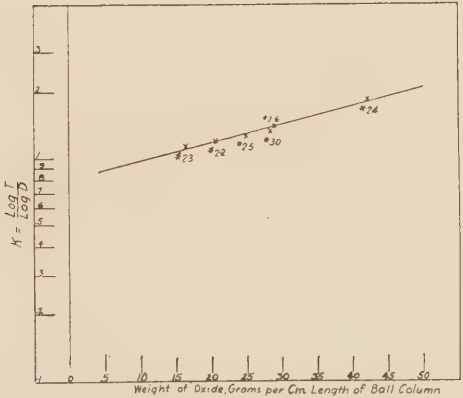
***The towel should be at the thermostat temperature.

The Removal of Hydrogen Sulphide From Gas



CURVE 1—Effect of Weight Per Unit Length of Column.
Weight-Surface Relations.

Results of Laboratory Experiments on Sulphiding Reaction



CURVE 2—Effect of Change in Weight-Surface Relations Upon K .

TABLE I
THE EFFECT OF CHANGES IN WEIGHT OF OXIDE PER UNIT SURFACE

TEST NO. 22 G _{A1}															
Avg. K C										Wt. of Oxide per cm. Wet Basis	H ₂ S gr./100 cu. ft.	Flow cu. ft./hr.	Temp. °C	% Rel. Humid. of Gas	% H ₂ O in Oxide
3-27-28	Min.	Time (T)	2.17	4.75	7.00	10.25	11.25	13.0	17.0	18.0	19.67	22.17			
	Cm. Dis-	tance (D)	1.3	3.5	4.7	7.0	7.5	8.7	11.3	11.5	13.0	14.3			
	log I														
	K =	log D													
			1.204	1.244	1.258	1.197	1.200	1.189	1.168	1.183	1.161	1.165			
									1.201	.886	.00208	.00136			
												.0632	38	75	
												360		34.5	
TEST NO. 23 G _{A1}															
3-28-28	T	1.83	4.0	6.25	9.33	12.17	14.25	16.75							
	D	1.6	4.1	5.9	7.5	9.2	10.4	11.4							
	K	1.289	0.983	1.104	1.108	1.128	1.137	1.159							
									1.132	1060	.00163	.00107			
												.0624	38	75	
												360		34.5	
TEST NO. 24 G _{A1}															
4-2-28	T	7.25	10.25	17.0	22.25	26.25	29.0	33.45	39.25	44.75	50.25				
	D	2.6	3.0	4.0	5.1	5.9	6.2	6.8	8.0	9.0	11.0				
	K	2.073	2.117	2.045	1.905	1.842	1.847	1.828	1.767	1.732	1.632				
									1.878	678	.00423	.00277			
												.0616	38	75	
												350		34.5	
TEST NO. 25 G _{A1}															
4-30-28	T	5.25	9.5	11.5	14.25	16.0	19.5	22.5							
	D	4.1	6.4	7.3	8.5	9.6	11.3	12.4							
	K	1.174	1.211	1.230	1.242	1.227	1.227	1.237							
									1.222	760	.00246	.00161			
												.0621	38	75	
												350		34.5	

Results of Laboratory Experiments on Sulphiding Reaction

TEST NO. 26 G_{A1}

5-7-28	Wt. of Oxide per cm.										Flow cu. ft./hr.	Temp. °C	% Rel. Humid. of Gas	% H ₂ O in Oxide				
Min. Time (T)	Avg. K		C	Wet Basis	Dry Basis					H ₂ S gr./100 cu. ft.								
2.58	5.0	10.33	12.75	15.0	17.75	21.5	24.75	27.75	30.5									
Cm. Dis- tance (D)	2.9	5.1	6.4	7.1	7.9	9.8	10.9	12.0	13.0									
log T																		
K=																		
log D	1.51	1.44	1.37	1.38	1.39	1.34	1.34	1.34	1.33									
1.48										1.391	735	.00289	.00189	360	.0597	88	75	34.5

TEST NO. 30 G_{A1}

11-22-28																				
T	2.0	3.0	4.5	7.25	11.0	15.17	20.67	23.83	28.5	30.5	35.0									
D	1.7	2.2	4.3	5.0	7.3	7.9	10.2	10.8	12.9	13.2	14.3									
K	1.309	1.392	1.031	1.231	1.209	1.316	1.304	1.331	1.310	1.322	1.338	1.31	697	.00287	.00188	350	.0676	38	75	34.5
Corrected for flow $C^1=697 \times (100+5.8)=736$																				

NOTE—During the six months' time between Test No. 26 and Test No. 30 the testing apparatus was modified in many details in order to simplify and otherwise improve the method of testing. Test No. 30 was made to check the results obtained with the new apparatus against those obtained with the original one. Curve 1 shows that the result falls on the curve. The hydrogen sulphide removal factor C, Test No. 30, was corrected for the 13.0% variation in the rate of gas flow over Test No. 26. From Curve No. 3 it was found that 1% increase in the flow caused 0.45% decrease in the value of C. Therefore, C should be increased 13x.45=5.8%. This method of correcting C is discussed later.

The Removal of Hydrogen Sulphide From Gas

THE EFFECT OF CHANGES IN THE RATE OF GAS FLOW

The study of the effect of variations in the rate of gas flow was made, as in the case of the weight per unit surface, primarily to determine the effect of this factor under conditions peculiar to the method of testing developed in this research. The conditions other than the rate of gas flow were maintained constant.

Curve 3 indicates that the hydrogen sulphide removal factor, C , is not inversely proportional to the rate of gas flow, i. e., the percentage removal* of hydrogen sulphide per unit weight of iron oxide is not inversely proportional to the rate of gas flow over the oxide. It is tentatively concluded from this that in gas plant practice, if the flow is increased 100%, the quantity of oxide need not be increased 100%.

The detailed data from which Curve 3 was obtained are shown in Table II.

THE EFFECT OF CHANGES IN HYDROGEN SULPHIDE CONCENTRATION

The tests on the effect of changes in the hydrogen sulphide concentration were made with gas in which the hydrogen sulphide varied from 20 grains to 620 grains per 100 cubic feet. The other variables were maintained as constant as conveniently possible. The weight was maintained constant in all but two of the tests by coating with oxide a quantity of the glass balls sufficient for a number of tests. This expedient has been used in the rate of flow tests also.

The slight variations in the rate of gas flow which occurred are not believed to be of sufficient importance to warrant the correction of the results for this variable.

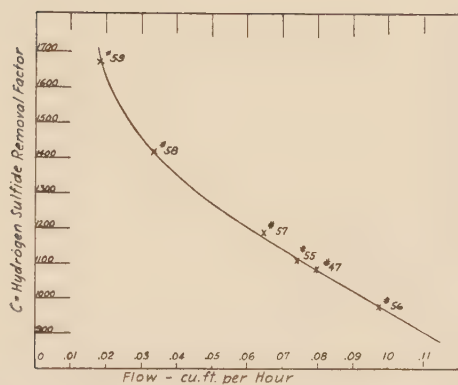
Curve 4a shows that the hydrogen sulphide removal factor, C , is not in a direct inverse relation to the concentration of hydrogen sulphide in the gas. This is the same type of curve as that obtained with variations in the rate of gas flow. This is shown by a comparison of Curves 3 and 4.

Comparison With Results of Dunkley and Leitch.—A comparison of the results of these tests with those of Dunkley and Leitch (D2) on the effect of hydrogen sulphide concentration on the activity of an oxide shows a striking similarity in the type of curve obtained. It will be seen, therefore, that Curve 4a verifies the conclusion of these authors that "the activity of an oxide is not inversely proportional to the concentration of H_2S in the gas coming to it." The oxide (No. 1) used by these investigators was believed to be a by-product of the dye industry.

The results of both these investigations indicate that less equipment per unit weight of sulphur removed is required in practice the higher the

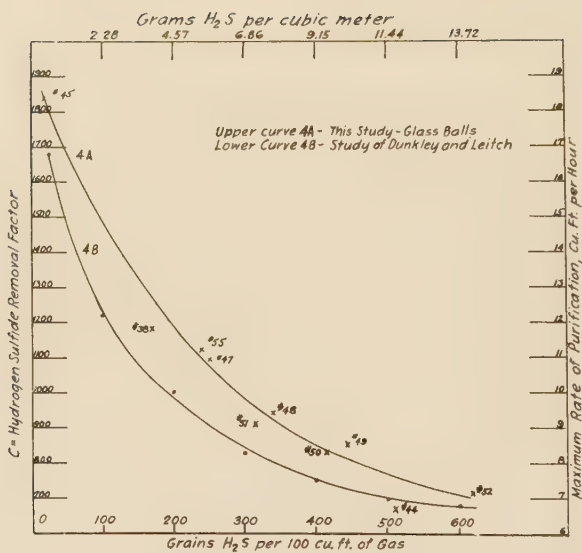
*Note: The percentage removal of hydrogen sulphide is defined in this research as the ratio of the inlet minus outlet to the inlet concentrations multiplied by 100.

Results of Laboratory Experiments on Sulphiding Reaction



CURVE 3—Effect of Variations in the Rate of Gas Flow.

The Removal of Hydrogen Sulphide From Gas



CURVE 4—Effect of Changes in Hydrogen Sulphide Concentration.

Results of Laboratory Experiments on Sulphiding Reaction

TABLE II
THE EFFECT OF CHANGES IN THE RATE OF GAS FLOW

TEST NO. 56 G _{A2}										TEST NO. 47 G _{A2}										TEST NO. 55 G _{A2}										TEST NO. 57 G _{A2}									

The Removal of Hydrogen Sulphide From Gas

TEST NO. 58 G_{A2}

	Wt. of Oxide			H ₂ S gr./100 cu. ft.	Flow, cu. ft./hr., 60° F., 30" hg.	Temp., °C.	% Rel. Humid. of Gas	% H ₂ O in Oxide
	Avg. K	C	Wet Basis	Dry Basis				
6-15-29								
T	3.0	4.25	7.0	8.5	10.25	14.5	18.5	21.0
D	2.2	2.7	4.0	4.4	5.0	6.9	9.3	9.9
K	1.395	1.458	1.402	1.446	1.567	1.386	1.309	1.328

TEST NO. 59 G_{A2}

	Wt. of Oxide			H ₂ S gr./100 cu. ft.	Flow, cu. ft./hr., 60° F., 30" hg.	Temp., °C.	% Rel. Humid. of Gas	% H ₂ O in Oxide
	Avg. K	C	Wet Basis	Dry Basis				
6-16-29								
T	7.5	14.75	20.25	25.5	29.0			
D	2.7	4.5	7.0	8.7	10.0			
K	2.055	1.79	1.545	1.496	1.462			

Results of Laboratory Experiments on Sulphiding Reaction

hydrogen sulphide concentration, i. e., if the hydrogen sulphide concentration is doubled the increase in apparatus and material required to take care of this impurity need not be doubled, but varies in some manner similar to that indicated by Curve 4.

From Curve 4a it would appear that an increase of 100% in the hydrogen sulphide concentration between 200 and 400 grains per 100 cubic feet only required an increase of 42% in equipment and material, or vice versa. The material would, of course, need to be changed more frequently.

The data obtained, with various hydrogen sulphide concentrations, are given in Table III.

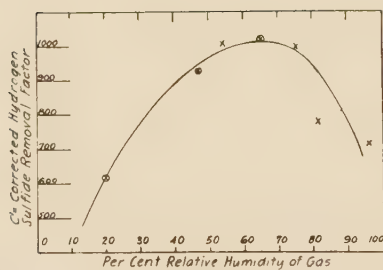
THE EFFECT OF CHANGES IN THE RELATIVE HUMIDITY OF THE GAS ON THE SULPHIDING REACTION

As pointed out in the presentation of the problem in Part I of this dissertation, it has been known for a long time that the water contained in the oxide, and the water in the form of steam admitted to the purifiers, has some effect upon the purification in practice. Former investigators, however, placed emphasis on the water content of the oxide and gave very little attention to the relative humidity of the gas stream. The present study of the kinetics of the sulphiding reaction gave major consideration to the humidity effect. The water content of an oxide varies according to the humidity to which it is subjected, other conditions being maintained constant, and by condensation or adsorption from the humid gas there is provided a water film of variable depth upon the surface of the oxide to serve as an important medium for chemical reactions.

Curve 5 shows the importance of maintaining the correct relative humidity if the optimum conditions for the reaction are to be maintained. The hydrogen sulphide removal factor, C' , discussed later, increased with increased humidity to a maximum at about 65% relative humidity, and then decreased as the humidity was further increased. Some of the possible explanations of this follow. The drying of the oxide as it was maintained in preparation for a long time at a humidity condition below 65% may have changed its structure somewhat. This change in structure may reduce the property of the oxide to remove hydrogen sulphide from the gas stream.

Another explanation is the extension of the liquid film to surfaces which are more plane (i. e., have less capillarity) as the humidity rises, thus giving a wetted surface of greater area. This effect may go on until it is neutralized by the creation of too deep a film on the surfaces of greater capillarity.

The Removal of Hydrogen Sulphide From Gas



CURVE 5—*Effect of Relative Humidities on Sulphiding Reaction.*

Results of Laboratory Experiments on Sulphiding Reaction

TABLE III
EFFECT OF CHANGES IN THE HYDROGEN SULPHIDE CONCENTRATION

TEST NO. 45 G _{A2}									
		Avg. K C		Wt. of Oxide per cm. Wet Basis		H ₂ S gr./100 cu. ft.		Flow cu. ft./hr. 60° F. 30" hg.	

The Removal of Hydrogen Sulphide From Gas

TEST NO. 48 G_{A2}

Avg. K C	Wt. of Oxide per cm.		H ₂ S gr./100 cu. ft.	Flow cu. ft./hr. 60° F. 30" hg.	Temp. °C	% Rel. Humid. of Gas	% H ₂ O in Oxide
	Wet Basis	Dry Basis					

6-5-29

T	4.1	5.5	7.1	8.75	10.0	12.0	14.0	15.25	17.0
D	5.7	6.9	9.2	10.0	10.7	14.2	16.6	17.5	19.7
K	0.811	.822	.882	.942	.972	.936	.939	.951	.950

TEST NO. 50 G_{A2}

Avg. K C	Wt. of Oxide per cm.		H ₂ S gr./100 cu. ft.	Flow cu. ft./hr. 60° F. 30" hg.	Temp. °C	% Rel. Humid. of Gas	% H ₂ O in Oxide
	Wet Basis	Dry Basis					

6-6-29

T	3.5	5.25	7.0	8.25	10.0	11.75	13.0
D	6.2	8.0	9.9	12.2	14.6	15.8	17.6
K	.687	.798	.848	.844	.858	.893	.885

TEST NO. 49 G_{A2}

Avg. K C	Wt. of Oxide per cm.		H ₂ S gr./100 cu. ft.	Flow cu. ft./hr. 60° F. 30" hg.	Temp. °C	% Rel. Humid. of Gas	% H ₂ O in Oxide
	Wet Basis	Dry Basis					

6-6-29

T	4.1	7.0	9.0	10.75	12.25	13.25	15.5
D	8.0	10.3	12.7	14.4	16.3	16.8	19.3
K	.679	.834	.864	.891	.897	.917	.921

TEST NO. 44 G_{A2}

Avg. K C	Wt. of Oxide per cm.		H ₂ S gr./100 cu. ft.	Flow cu. ft./hr. 60° F. 30" hg.	Temp. °C	% Rel. Humid. of Gas	% H ₂ O in Oxide
	Wet Basis	Dry Basis					

5-4-29

T	1.75	3.25	6.0	8.0	10.75	12.5	13.25
D	3.2	5.0	8.6	12.2	14.5	17.0	17.6
K	.431	.731	.832	.831	.888	.891	.902

TEST NO. 52 G_{A2}

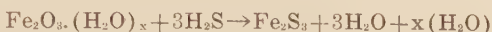
Avg. K C	Wt. of Oxide per cm.		H ₂ S gr./100 cu. ft.	Flow cu. ft./hr. 60° F. 30" hg.	Temp. °C	% Rel. Humid. of Gas	% H ₂ O in Oxide
	Wet Basis	Dry Basis					

6-8-29

T	2.25	3.8	5.0	6.0	6.75	8.0	9.25	10.75	11.5
D	5.7	8.7	10.5	12.3	12.9	14.7	16.5	18.3	19.4
K	.446	.617	.684	.713	.746	.774	.795	.816	.824

Results of Laboratory Experiments on Sulphiding Reaction

Water is one of the products in the reaction



so that its removal by a gas stream of low humidity will tend to displace the reaction to the right and so increase the rate of the sulphiding reaction. As the humidity is increased above 65% the capacity of the gas to carry away the water formed by the reaction is decreased, which in turn decreases the rate of the sulphiding reaction.

From the results* obtained in this investigation it appears that the optimum relative humidity under the conditions tested is about 65%.

Calculation of Corrected "Hydrogen Sulphide Removal Factor, C".—As previously stated, in order to make a comparative study of the effect of humidity it was necessary to correct the value of the hydrogen sulphide removal factor, C, obtained from the data of a particular test to a standard set of conditions. These conditions are as follows: weight per unit surface (dry basis)=0.0007 grams per cm., hydrogen sulphide concentration=250 grains per 100 cubic feet, rate of gas flow at 60° F. and 30" Hg.=0.08 cubic feet per hour, temperature=38° C. (100.4° F.).

The value of C obtained as previously indicated was corrected for the variation in the weight per unit surface by means of an extrapolation factor obtained from Curve 1. While this method leaves something to be desired, it is believed to be of sufficient accuracy within the ranges under consideration. The correction for the variation in the rate of gas flow was obtained in a similar manner from Curve 2. All the other variables were maintained constant, therefore no corrections for these were necessary.

These corrections are as follows:

(a) $\pm 1\%$ variation from standard conditions in the weight per unit surface (0.0007 grams per cm.) causes $\pm 0.5\%$ variation in C.; (b) $\pm 1\%$ variation from standard conditions in the rate of gas flow (0.08 cubic feet per hour) causes $\pm 0.45\%$ variation in C.

The derivation of the corrected factor, C', is illustrated, using the data from Test No. 74:

$$(a) \text{ Correction factor for weight} = 1 + \frac{0.00077 - 0.00070}{0.00070} \times .5 = 1.05$$

$$(b) \text{ Correction for flow} = 1 + \frac{0.0774 - 0.0800}{0.0800} \times .45 = 0.985$$

$$C' = \frac{C \times (a) \times (b)}{893 \times 1.05 \times 0.985} = 924$$

*The results indicated by Test No. 78 on zero relative humidity are not completely comparable to those shown in the other tests because the sample of oxide used in this test was maintained at room temperature during preparation (approximately 80° F.) while the sample used in the other tests was maintained at 100° F. in the cabinet thermostat. However, the trend is comparable.

TABLE IV
THE EFFECT OF CHANGES IN THE RELATIVE HUMIDITY ON THE SULPHIDING REACTION
TEST NO. 71 Gc

				Uncor- rected C	Wt. of Oxide per cm. Wet Basis		H ₂ S gr./100 cu. ft.	Flow cu. ft./hr. 60° F 30" hg.	Temp. °C	% Rel. Humid. of Gas	% H ₂ O in Oxide
				K	20 cm.						
				Mean	10 cm.						
				.821	.740	.903					
6-30-29											
Min.											
Time (T)											
1.75 2.25 3.0 4.0 5.0 6.0											
Cm. Dis-											
tance (D)											
9.0 10.0 11.1 14.0 16.2 18.8											
Log T = K											
Log D											
.255 .352 .456 .526 .577 .609											
				.491	.352	.630	.723	.00095	.00068	.0806	250
										C ¹ =723×0.984×1.003=714	
										95.8	28.8

TEST NO. 65 Gc

T	1.25	1.75	2.25	3.5	4.0	4.75																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																							</
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Results of Laboratory Experiments on Sulphiding Reaction

TEST NO. 73 Gc

7-2-29		Mean	K 10 cm. 20 cm.	Uncor- rected C	Wt. of Oxide Wet Basis	Dry Basis	H ₂ S gr./100 cu. ft.	Flow cu. ft./hr. 60° F. 30" hg.	Temp. °C	% Rel. Humid. of Gas	% H ₂ O in Oxide
T	2.5	3.25	4.4	5.5	7.0	8.0	9.3	10.3	11.5	12.5	
D	3.7	6.8	8.7	10.0	11.7	13.0	14.7	16.0	17.1	19.0	
K	.526	.615	.684	.740	.791	.810	.830	.841	.861	.858	.821
			.740	.903	856	.00121	.00096	.0780	38	54	20.3
							C ¹ =856×1.186×0.989=1004				

TEST NO. 74 Gc

7-3-29		Mean	K 10 cm. 20 cm.	Uncor- rected C	Wt. of Oxide Wet Basis	Dry Basis	H ₂ S gr./100 cu. ft.	Flow cu. ft./hr. 60° F. 30" hg.	Temp. °C	% Rel. Humid. of Gas	% H ₂ O in Oxide
T	1.75	3.0	3.75	4.75	5.5	6.5	7.5	9.0			
D	4.4	7.4	9.2	11.0	13.0	14.6	16.9	19.0			
K	.378	.550	.595	.650	.664	.698	.714	.746			
		.687	.621	.754	.893	.00095	.00077	.0774	38	47	19.0
							C ¹ =893×1.05×0.985=924				

TEST NO. 77 Gc

57 7-10-29		Mean	K 10 cm. 20 cm.	Uncor- rected C	Wt. of Oxide Wet Basis	Dry Basis	H ₂ S gr./100 cu. ft.	Flow cu. ft./hr. 60° F. 30" hg.	Temp. °C	% Rel. Humid. of Gas	% H ₂ O in Oxide
T	1.0	2.0	3.0	3.5							
D	3.0	8.0	14.5	19.0							
K	.334	.411	.425								
		.399	.371	.427	.725	.00067	.00055	.0719	38	20	17.8
							C ¹ =725×0.893×0.954=618				

TEST No. 78 Gc *

7-10-29		Mean	K 10 cm. 20 cm.	Uncor- rected C	Wt. of Oxide Wet Basis	Dry Basis	H ₂ S gr./100 cu. ft.	Flow cu. ft./hr. 60° F. 30" hg.	Temp. °C	% Rel. Humid. of Gas	% H ₂ O in Oxide
T	2.5	4.0	5.0	5.5	6.0						
D	7.5	13.2	16.3	18.5	19.4						
K	.455	.536	.578	.585	.604						
		.556	.494	.619	.806	.00084	.00069	.0763	38	Approx. 0	18.1
							C ¹ =806×0.993×0.979=784				

*See note page 53.

The Removal of Hydrogen Sulphide From Gas

Material and Saturated Solutions Used to Obtain Various Humidities.

Material	% Relative Humidity	Reference
Phosphorous Pentoxide, P_2O_5	0%	(I3)
Zinc Chloride, $ZnCl_2 \cdot 1\frac{1}{2}H_2O$	10%*	(I3)
Potassium Acetate, $KC_2H_3O_2$	20%*	(I3)
Chromic Acid, CrO_3	35%*	(I3)
Potassium Sulphocyanide, $KCNS$	47%*	(I3)
Sodium Chromate, $Na_2CrO_4 \cdot 2H_2O$	52%*	(I3)
Ammonium Nitrate, NH_4NO_3	53.9%	(A4)
Magnesium Acetate, $Mg(C_2H_3O_2)_2 \cdot 4H_2O$	65%*	(I3)
Sodium Chloride, $NaCl$	74.9%	(A4) (L1)
Potassium Chloride, KCl	81.6%	(A4) (L1)
Potassium Sulphate, K_2SO_4	95.8%	(A4) (L1)
Water, H_2O	100%	

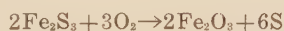
The humidity values vary with the temperature, but are believed to be sufficiently approximate at 38° C. for the comparisons made in this dissertation. The change from one temperature to another is dependent upon changes in the solubility, ionization and other factors and cannot be gone into here. References: Adams and Merz (A4), Leopold and Johnston (L1).

*Relative humidities marked * were obtained from the International Critical Tables (I3) and apply at 20°C. The values not so marked apply at 38°C.

CHAPTER III

RESULTS OF LABORATORY EXPERIMENTS ON THE REVIVIFICATION REACTIONS

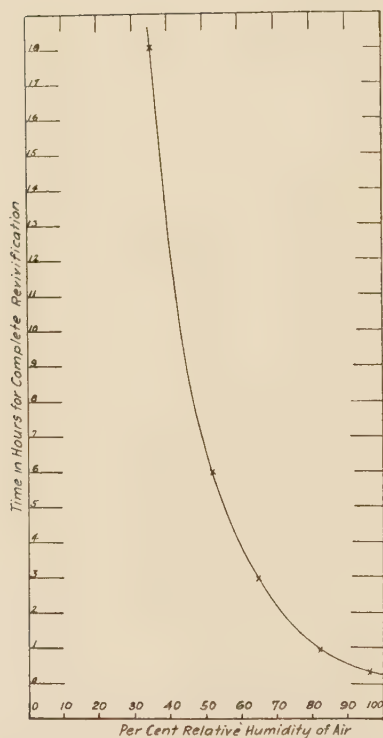
From the standpoint of plant practice, the relations between the humidity and the rate of revivification developed in this dissertation are believed to be of particular interest. One form of the revivification reaction often given is:



Although this equation does not show water as a reactant, it will be shown that the humidity of the oxygen containing gas is a most important controlling factor.

During the study of this reaction several attempts were made to use the same color test that was applied to the fouling of iron oxide by hydrogen sulphide. This proved impracticable because the color change took place gradually throughout the entire length of the testing tube instead of showing a sharp distinction between the revived and unrevivified material. The revivifying reaction is very slow. Thus it was noted that, in a preliminary test of the revivification of a fouled sample of the oxide (G_A) at 75% relative humidity, the coating on the balls changed from black to reddish brown only after about twenty minutes, whereas the formation of the black sulphide from the brown oxide in the sulphiding reaction appeared to be almost instantaneous. It thus appears that in the commercial practice using the continuous revivification in place the rate of revivification is the controlling factor in the cycle. This was investigated further by placing the sulphide coated balls in the testing tube previously mentioned. The concentration of the oxygen in the atmosphere used for revivification of these balls was varied between 5% and 20% in a series of experiments by mixing with purified gas the air prior to its passage over the material. These variations of oxygen concentration appeared to have no appreciable effect on the rate of revivification of the sulphide. Likewise, variation in the rate of the flow of the oxidizing gas, amounting to about five hundred times (approximately 0.01 cubic feet to 5.0 cubic feet per hour), showed no noticeable effect. The above results appear to indicate that the controlling factor in the oxidation of ferric sulphide is some condition upon its surface rather than the rate of diffusion across the gas film surrounding it.

The Removal of Hydrogen Sulphide From Gas



CURVE 6—Effect of Relative Humidities on Revivification Reaction.

(NOTE—Test at 20% humidity only partially revived after 5,780 hours. Test at 10% humidity gave no indication of revivification after about one year.)

Results of Laboratory Experiments on Revivification Reaction

THE EFFECT OF CHANGES IN THE RELATIVE HUMIDITY OF THE GAS ON THE REVIVIFICATION REACTIONS

In order to study the effect of variations in the relative humidity on the revivification reactions a sample of iron oxide (G_A) was coated on a number of the glass balls in a very thin film as previously described. The oxide was then completely sulphided by passing gas containing hydrogen sulphide over it. Four of these iron sulphide coated balls were then placed in each of the desiccators containing the various saturated salt solutions for maintaining the various relative humidities (0% to 100%) at 38° C. The time required for the humid air in the desiccator to change the color of the black iron sulphide to the brownish red iron hydrate was taken as a measure of the rate of the oxidation or revivification reaction.

The results of Test R1, Table V, on oxide G_A show that at 38° C. the rate of this reaction increased rapidly as the relative humidity was increased. Further, several of the sulphided balls used in this test were allowed to oxidize at 68% humidity and a temperature of 23.5° C. Even with this reduction in temperature (14.5° C.) the sulphide revived faster at 68% humidity than at humidities below 20% at 38° C.*

Test R2, which showed the most striking results, was made on iron hydrate, $G1$,** in a similar manner to Test R1. The very considerable differences in the rate of revivification at the various humidities are clearly shown by Curve 6, which was plotted from the data detailed in Table V. After 8 months the sulphide maintained in an atmosphere of substantially pure air at 10% relative humidity and 38° C. still appeared to be as black as when first placed in the desiccator. At 20% humidity the observations indicated that some revivification had taken place after 5,780 hours. A slight brown coloration was first noted on the balls after this time had elapsed.

To further verify the effect of various humidities of the gas on iron oxide purification in practice, Test R3 was made on a material, originally a bog ore, which had been in use two years under gas plant conditions. This sample was taken from the first box of a purifier series while this was being dumped. Parts of it were placed in the desiccators at the various humidities and at 38° C. The results of this test are shown in Table V. It will be seen that the same trend was obtained as with the synthetic hydrate, G , only differing in degree, that is, the intensity of the color change and the time required to effect this change were different, probably due to the deposition of tar and the formation of the unrevivifiable iron compounds*** while in the purifier box.

* (0.67 hours were required at 68% and 23.5° C. and 1.33 hours at 10% and 38° C.)

** $G1$ was a yellow form of iron hydrate prepared by the method of Krause ($K1$) from hydrate G by allowing the latter to stand under one normal sodium hydroxide solution for one month. This was then washed free of the solution and air dried to 16.8% moisture (determined by ignition).

***Such as, perhaps, iron disulphide (Pearson $P1$) or other iron salts.

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It appears, therefore, that the optimum relative humidity for revivification of iron sulphide is 100%. Data will be offered in a later section, however, to show that the excessive deposition of moisture is very undesirable and must be avoided. This can best be done by using a humidity approximately but slightly less than 100%.

TABLE V

THE EFFECT OF CHANGES IN THE RELATIVE HUMIDITY ON REVIVIFICATION REACTION

3-23-29			
TEST R1-G _A			
Relative Humidity %	Relative Time for Revivification Hours *	Original %H ₂ O in Oxide	Temp. °C.
96%	0.08	28%	38°
75%	0.12	28%	38°
65%	0.17	28%	38°
35%	0.33	28%	38°
20%	0.67	28%	38°
10%	1.33	28%	38°
68%	0.67	28%	23.5°
4-19-29			
TEST R2-G ₁			
100%	0.25	16.8%	38°
96%	0.33	16.8%	38°
82%	0.92	16.8%	38°
65%	3.00	16.8%	38°
52%	6.00	16.8%	38°
35%	18.00	16.8%	38°
20%	(Partial) 5780.00 **	16.8%	38°
10%	No revivification during test	16.8%	38°
9-1-29			
TEST R ₃ (Bog Ore) ***			
Relative Humidity %	Color	Total Change After 4 Months	Temp. °C.
100%	Brownish Gray	Considerable	38°
96%	Brownish Gray	Considerable	38°
82%	Brownish Gray	Considerable	38°
52%	Black Trace of Brown	Some	38°
47%	Grayish Black	Slight	38°
35%	Grayish Black	Slight	38°
20%	Black Trace of Gray	Very slight	38°
10%	Black Trace of Gray	Very slight	38°
0%	Black	None	38°

*Note: All figures on time or color change are accurate to about $\pm 10\%$.

**Note: See previous discussion.

***Note: Sample of sulphided natural iron oxide which had been in plant use two years. Color change difficult to see because of impurities such as deposited tar.

CHAPTER IV

COMPARISON OF OXIDE CHARACTERISTICS

In the early stages of this investigation a preliminary study was made on various samples of iron oxide by the glass ball test previously described in Part II, Chapter I. The primary aim of this study was to determine, if possible, any peculiar characteristics in the various oxides available. Curve 7 and Table VI show the results of these tests. Although not completely comparable because the conditions varied from test to test, an examination of the various curves shown suggests that each oxide may give curves having a characteristic form peculiar to that oxide, although the exact location of the curve may depend upon the individual history and condition of the test samples.

Thus it will be noted that variations in (1) the gas flow, (2) the hydrogen sulphide concentration within small limits (330 to 360 grains per 100 cubic feet of gas), (3) the humidity, (4) the temperature (20° to 30° C., 68° to 86° F.), and (5) the weight of oxide supported on the glass ball per unit surface, does not seem to change the general form or slope of the curves obtained from tests on any one oxide. Curves for different oxides, however, even cross each other in two points as shown. It thus appears that the test shows not only the variation of the oxide under varying conditions, but also some structural characteristic. Thus, Tests 2A and 3A gave the same characteristic type of curve. This same type was given by Test 8-C, conducted upon another sample of the same oxide. This indicates the similar structure of the two samples, A and C.

Test 6B1 gives the results obtained on a natural iron oxide which had been previously sulphided slightly and then revived.

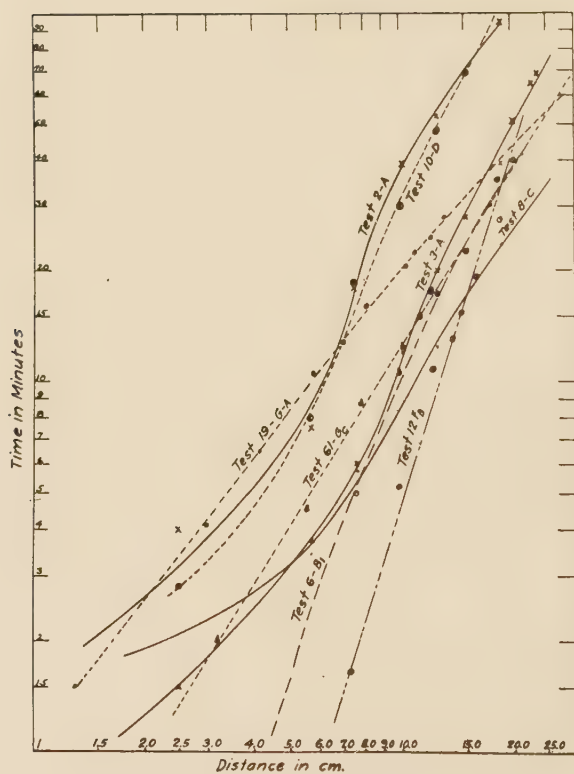
Test 10-D shows the results on another oxide.

The oxide used in Test 12-Fb was precipitated from the chloride and contained a trace of ferric chloride. Its curve is similar to that of oxide, D, in that it appears to be a straight line on log-log co-ordinate paper.

The oxide precipitated from the nitrate also shows a nearly straight line relation between the logarithm of time and logarithm of the distance, but with an entirely different slope. Test 19-G_A was made with the fresh oxide, Test 61-G_C after it had been aged 15 months.

A test on "Baker Analyzed" oxide, E, showed no activity whatsoever after 24 hours' contact with hydrogen sulphide. This is evidently a fused oxide, as its water content was only .075%. Moistening it had no

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CURVE 7—Characteristic Curves of Various Oxides.

Comparison of Oxide Characteristics

effect on its activity. This verifies the results which Weyman (W4) and other investigators obtained with a strongly ignited oxide.

It is believed, from the above results, that considerable information on the characteristics of different oxides can be obtained by further investigations utilizing such test and curves.

TABLE VI
COMPARISON OF OXIDE CHARACTERISTICS

TEST 2-A										
T	4.0	7.5	18.0	39.0	52.5	70.0	95.0	114.0		
D	2.5	5.8	7.6	10.2	12.7	15.2	18.8	20.3		
TEST 3-A										
T	1.5	3.7	6.0	12.0	20.0	28.0	39.5	51.0	64.5	68.5
D	2.5	5.8	7.6	10.2	12.7	15.2	18.8	20.3	22.9	23.8
TEST 6-B ₁										
T	5.0	15.0	17.2	22.5	27.5	40.0				
D	7.6	11.4	12.7	15.2	18.8	20.3				
TEST 8-C										
T	2.1	3.4	5.7	8.8	12.4	17.2	23.7			
D	2.5	5.8	7.6	10.2	12.7	15.2	18.8			
TEST 10-D										
T	2.8	8.0	18.3	30.0	47.8	69.2				
D	2.5	5.8	7.6	10.2	12.7	15.2				
TEST 12-F _B										
Precipitated from chloride, F _B .										
T	1.6	6.2	10.8	13.0	15.2	19.3	35.5			
D	7.0	10.0	11.8	14.0	14.7	16.3	18.0			
TEST 19-G _A										
Material precipitated from nitrate, G _A .										
T	1.5	4.1	6.5	10.5	12.7	16.0	20.2	22.2	24.7	28.0
D	1.3	3.0	4.2	5.9	7.1	8.2	10.5	11.1	12.2	13.3
TEST 61-G _C										
G _A aged one year, G _C .										
T	0.7	2.0	4.5	8.7	10.5	12.2	17.5	22.7	30.0	
D	1.5	3.2	5.6	7.9	10.0	10.3	12.2	15.2	17.6	

CHAPTER V

THE APPLICATION OF HUMIDITY CONTROL TO COMMERCIAL PURIFICATION ON A LARGE SCALE

THE EFFECT OF CHANGES IN THE RELATIVE HUMIDITY OF THE GAS

The effect of variations in the relative humidity on the removal of hydrogen sulphide from manufactured gas, particularly coal gas, by means of iron oxide was studied at the plant of a large public utility company.

This study was divided into two parts. In the first, the importance of variations in the relative humidity as a factor in the economic and efficient operation of the commercial purifying system was established. In the second, the attainment and maintenance of an increased efficiency through the control of the relative humidity and temperature were sought. That such increased efficiency was obtained and held will be shown by detailed data to be presented later.

APPARATUS

Hygrometer.—The instrument used to measure the humidity of the gas entering and leaving the various purifiers was of the wet and dry bulb type, as shown in the photograph. The dry bulb side was connected to the gas sample cock by means of a short piece (6") of rubber tubing.

Hygrometer Operations and Precautions.—It required from 5 to 20 minutes for the apparatus to come to equilibrium, depending upon the difference in temperature between the inside of the jug when first connected and the temperature of the gas to be tested. In order to expedite the testing, at least four hygrometers should be available. With this number, the worker can permit the first to come to equilibrium while the others are being attached to other sampling points and hydrogen sulphide determinations are being made.

According to the discussion on hygrometry in the Proceedings of the Physical Society (P4), the linear rate of flow of gas over the wet bulb should be at least 10 feet per second. In this hygrometer the volumetric rate should be at least 18 cubic feet per hour. For the best results, the errors of the thermometers must be determined (and all corrections applied), readings to tenths of degrees should be possible, the wick of the wet bulb should be kept clean. If a glass wool filter is used, care must be taken that this does not become saturated with water. No filter should be used when determining the humidity of a nearly saturated gas because of the condensing tendency of the water vapor in the

Application of Humidity Control to Commercial Purification

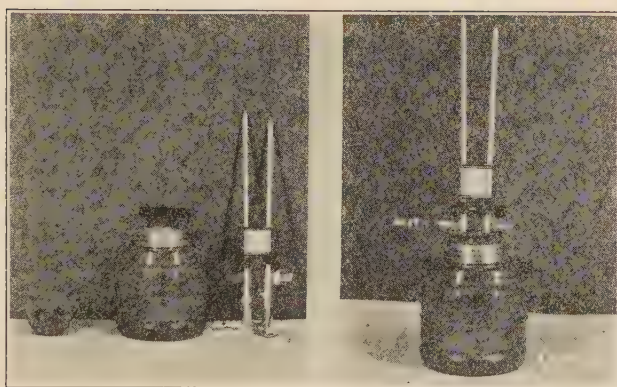


FIGURE 5—*Hygrometer.*

The Removal of Hydrogen Sulphide From Gas

gas, especially if the temperature of the jug is slightly lower than that of the gas being tested. To reduce radiation from the glass parts of the U-tube which extend above the rubber stopper, these are insulated either by split rubber tubing or preferably by winding these parts with asbestos cord.

Under good conditions, reproducible results can easily be obtained, but an absolute accuracy of within 2% cannot be assured. If care of the wick and attention to the rate of flow are neglected, errors greater than 5% may develop under apparently normal conditions. If either the relative humidity or the temperature is low, or if the relative humidity approaches 100%, the errors may be larger than 10%. A piece of string is tied around the wick to prevent the syphoning effect of the gas from sucking the water from the thermos jug over the wet bulb. Care must be taken to keep the string in the proper place in the hole in the U-tube. Distilled water should be used in the thermos jug. This should be at a temperature near that of the gas, and only sufficient water should be employed to insure that the wick is thoroughly wet at all times. About 10 cubic centimeters, in addition to that required to saturate the wick, should be sufficient for each test. The U-tube, water and the excess wicking should be so arranged that there is little heat interchange of consequence between the U-tube and the excess water and wicking. This can be done by placing the U-tube above and well out of contact with the excess wicking.

The observations made in connection with the use of the above apparatus are (1) dry bulb temperature, (2) wet bulb temperature, (3) barometer, (4) the pressure on the purifiers, and (5) the temperature of the oxide.

Care must be taken to insure that the samples and temperature observations are representative, and that no condensation occurs in the sample line, which should be very short.

The relative humidity at the hygrometer is determined by the temperature readings, using appropriate tables, such as are given in the Smithsonian Physical Tables (S14). A convenient alignment chart for use in humidity determinations has been given recently by Brooks, of the Bureau of Standards (B5).*

It should be noted that the hygrometer readings give the relative humidity of the gas at the hygrometer. If the temperature and pressure of the gas at this point are substantially the same as it is on the oxide, it also gives the relative humidity on the oxide. If, however, the pressure and temperature are different, it is necessary to calculate the humidity on the oxide from the above observations. To do this, a vapor pressure table for water should be at hand. From this table the vapor pressure of the water at the hygrometer is calculated as follows:

*These apply, of course, only to gases having the same heat capacity per unit volume as does air. If the volumetric heat capacity differs markedly from that of a diatomic gas, further corrections must be made. See Chapter XIV, Reference (W2).

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Assume relative vapor pressure at hygrometer to be $A_1\%$, gas pressure at hygrometer N_1 in total absolute units and at the oxide, N_2 , in the same units, also that the saturated vapor pressure of the water at the temperature corresponding to the dry bulb of the hygrometer (t_1 , absolute units) is V_1 , and the vapor pressure at the temperature corresponding to the oxide (t_2 absolute units) is V_2 . Then the relative vapor pressure on the oxide ($A_2\%$) is found as follows:

$$A_2 = \frac{A_1 \times V_1 \times \frac{N_2 \times t}{N_2 \times t_2}}{V_2}$$

In many cases the corrections will be so small as to be unnecessary, and when the operations become routine it will probably be found that the number of observations and calculations made can be reduced. Thus it may be found that the pressure corrections are unnecessary.

The study should emphasize, however, that the temperature and the humidity of the gas on the oxide are the determining factors, and that these should be known.

Humidity and hydrogen sulphide determinations were made daily on each box. The temperature and humidities were controlled by the use of live and exhaust steam and by a readjustment of the steam valves daily.

Other Apparatus—The hydrogen sulphide concentrations were determined by the Tutwiler method (G2) and the lead acetate stain paper test (G2). The analyses for the percentages of oxygen in the gas were made with the Haldane apparatus, as described by Burrell (B4). The pressure was measured by an ordinary U-tube manometer. Such readings of the gas rate through the purifiers as were possible were made by means of the Thomas meter. This meter has been described by Penney and Fechleimer (P5).

EXPERIMENTAL RESULTS

Tests to Determine Importance of Relative Humidity and Temperature Regulation.—As previously stated, the study was first directed to the determination of the importance of variations in the relative humidity of the gas as a factor in the operation of the purifying system.

It will be recalled that the laboratory tests have shown that the optimum relative humidity for sulphiding at 100° F. is about 65% with the oxide studied, while the best humidity for complete revivification approximates 100%. Moreover, it was shown that the sulphiding occurred very rapidly, while the revivification is relatively very slow. In the plant under study, continuous revivification in place was practiced, i. e., the oxygen content of the gas was at all times slightly above 0.4%. From this information it was predicted, therefore, that the revivifying

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condition, demanding a high humidity, would here control (H4), and the data to be presented amply support this expectation.

Continuous revivification in place with the oxygen content, 0.4% to 1%, presents a number of advantages, among which is the maintenance of uniform moisture conditions at all times, whereas when the sulphiding and revivification reaction are separated, the difference in the optimum moisture conditions may lead to caking of the oxide and preferred passages.

Description of Purifiers.—Of the two more inefficient series of purifiers in the plant, one (H) was chosen for this study. Trouble had been encountered with this series for several months in the late spring. This series was chosen because it was believed that the effect shown by controlling an inefficient series would be a clear indication of the effect to be expected on the other series. The results were verified to some extent by later tests made on series (G), which appeared to be the most efficient series. The summarized results of these tests are shown on Curve 14 and will be discussed later.

Each of the purifying boxes in Series (H) were of the 6,000-bushel type described in Part I, Chapter I. The box through which the gas passed first in a series was designated as the box in position No. 1, the second box as the box in position No. 2, and so on. The iron oxides in these boxes consisted of "A," a by-product of the aluminum industry, and "B," a natural iron oxide or bog ore, principally the latter. The distribution of these materials throughout the various boxes and the time the oxide had been in service is given in Table VII.

The other series tested were all of the same type and capacity, with the exception of Series (I). The boxes in the latter were of 18,000-bushel capacity.

TABLE VII

DATA ON MATERIAL IN PURIFYING BOXES

Box	Box in Service* Months	Material in Box	Capacity per Box Bushels of Sponge‡	Dimensions of Box Feet
<i>Series G</i>				
1	22.5	1 layer used B† 2 layers new B	6,000	21×35×12
2	14.5	1 foot shavings, 9 feet new B		
3	8.0	1 layer new B 2 layers oxide A		
4	6.0	2 layers new B 1 layer oxide A		

*At the start of this study.

†One layer consisted of material which had been revivified out of place once.

‡Sponge is oxide mixed with shavings. One bushel of A sponge contained approximately 20 pounds of A material coated on pine shavings. One bushel of B sponge contained approximately 30 pounds of oxide. Lime, 2 per cent as CaCO₃.

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Series H

Box	Box in Service *	Material in Box	Capacity per Box Bushels of Sponge	Dimensions of Box Feet
	Months			
1	19.0	1 foot shavings, 9 feet new A	6,000	21×35×12
2	14.5	1 foot shavings, 9 feet new B		
3	11.5	2 layers new B		
		1 layer new A		
4	6.3	2 layers new B		
		1 layer new A		

Series I

1	23	2 layers A	18,000	45×55×12
		1 layer B		
2	21	2 layers new B		
		1 layer new A		
3	14	1 layer new B		
		2 layers new A		
4	4	2 layers new A		
		1 layer new B		

In all series the inlet was at the bottom of a box and the outlet at the top. The humidity was measured on the inlet gas on all boxes except those in position No. 1, on which it was measured on the outlet.

Discussion of Curves.—The results of these tests are shown in Curves 8 to 12 and in Table VIII. Curves 8, 10 and 12 show the results of Series (I); Curve 9 those of Series (H). Curve 11 combines these results.

It will be seen that under conditions of this investigation, which was made during the summer months, the relative humidity is the most important factor affecting the removal of hydrogen sulphide from the gas by means of iron oxide. Within the limits of the tests, variations in the other factors, such as temperature, rate of gas flow, concentration of hydrogen sulphide, and the steam and air added to the purifiers, have only secondary effects on the per cent hydrogen sulphide removed * per box. This is indicated by Curves 8 and 12, which show no definite trend of these factors, the points being scattered at random. Curves 8, 9, 10 and 11 show a very marked trend in the relative humidity factor against the per cent hydrogen sulphide removed. The box in position No. 1 of (I) series was the only one of six boxes which does not show this definite trend. This may be due to the non-uniformity of the gas-steam mixture entering this box. Further, it is probable that the in-

*The per cent hydrogen sulphide removed per box or the efficiency of a box is defined as the percentage of this constituent removed from the gas in flowing through the box, i.e., the ratio of the grains of hydrogen sulphide per 100 cubic feet in the inlet minus outlet to the grains in the inlet gas multiplied by 100.

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terior temperature of the box in this position was higher and the humidity lower on the oxide surface than was shown at times on the outlet tests, i.e., the interior oxide temperature-humidity effect varied, which was especially hard to follow in this case, because of the large size of the box, variations in gas flow, in heating, and the comparatively large differences in the entering hydrogen sulphide concentration. Another explanation is the possible unequal division of the gas flow.

From Curve No. 11 it may be estimated that a drop of 1% in the relative humidity causes a reduction of about 3% in the efficiency of all the boxes of (H) series, 2% in the efficiency of the box in position No. 2 of (I) series, and about 1% in the case of the box in No. 3 of (I) series. This shows not only the important effect of the humidity, but also the reduction of this effect in the large boxes. This is further substantiated by the following table: *

Box in Position	Indicated Maximum Efficiency	
	Series H	Series I
No. 1	65%	
No. 2	100%	83%
No. 3	100%	100%
No. 4	100%	100%

It will be seen that the efficiency of the small 6,000-bushel purifier boxes of (H) series in position No. 2 was 17% greater than that of the large 18,000-bushel box of (I) series in position No. 2.

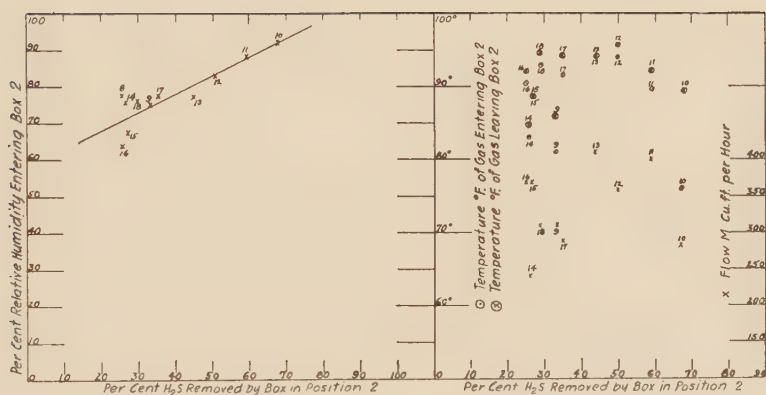
Curve 12 shows the variation with time of a number of the factors affecting purification using an 18,000-bushel purifier in position No. 1 of Series I. This chart illustrates the complicated conditions in the purifiers. These complications confirm the greater importance of humidity control over that of the other factors because, even with such variable conditions, the efficiencies show a very definite trend with the relative humidities.

The optimum relative humidity for the gas containing 0.8% oxygen appears to be about 98%, i. e., the maximum efficiency is obtained when the gas is nearly saturated with water vapor. Although 100% saturation is desirable theoretically, in practice a slight decrease in temperature will cause the deposition of excess moisture. This excess, in one case, shown in Curve 9, reduced the efficiency 40%.

A given increase in temperature may improve the operation of an inefficient purifier much more than the same increase may improve an efficient purifier. In one case of an inefficient series, E, one of the boxes increased in efficiency from 13% at 81° F. to 57% at 93.5° F., while in G, an efficient series, the box in position No. 1 only increased from 24% at 82.9° F. to 36% at 92° F. These results are not conclusive because of other varying conditions. However, it was indicated

*Data obtained from Curves 9 and 10.

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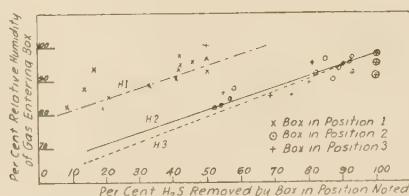


8A—Percent H_2S Removed vs. Percent Relative Humidity.

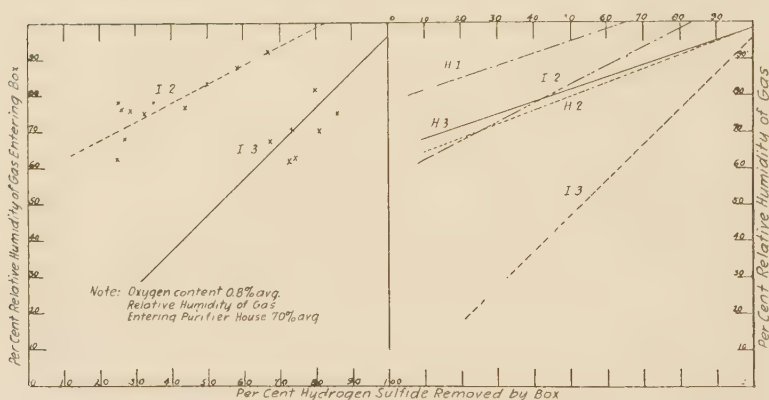
8B—Percent H_2S Removed vs. Time of Contact (x) vs. Temperature (o).

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by general observation that the operating temperature should not be allowed to fall below 90° F. in the case of an inefficient box or below 80° F. in the case of an efficient box.



CURVE 9—Efficiencies of Purifiers, Series H.



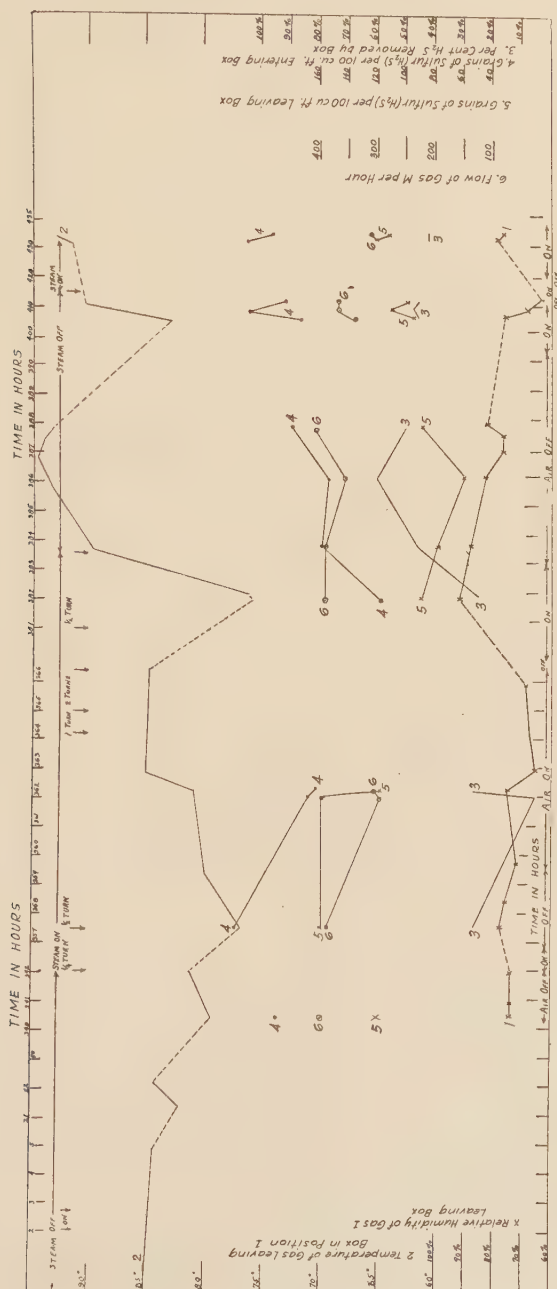
CURVE 10—Series I, Boxes in Positions 2 and 3.

CURVE 11—Series H, Boxes in Positions 2 and 3; Series I, Boxes in Positions 2 and 3.

While the data on temperature are rather incomplete, the writer favors a temperature of 95°F., as a result of both his own observation and because of the statements in the literature as already given in Part I, Chapter IV.

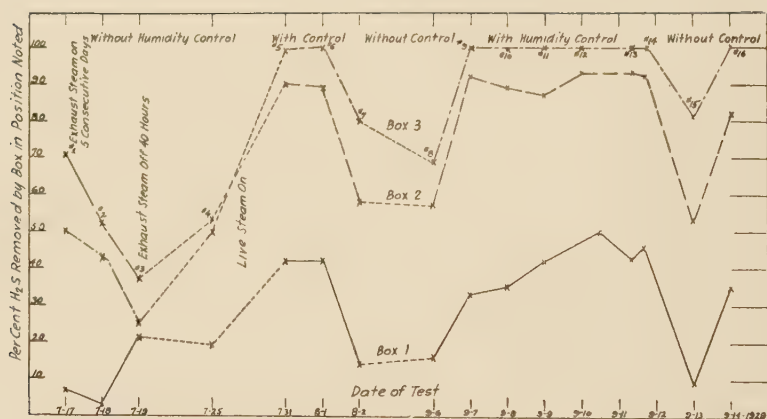
TESTS INVOLVING THE CONTROL OF HUMIDITY AND TEMPERATURE

From the results shown above it was decided that the relative humidity at the oxide surface should be maintained at 96-98% and the temperature at about 95°. The maintenance of approximately these optimum conditions, particularly that of the humidity, was accomplished by varying the quantity of live and exhaust steam admitted to the gas entering the first box of a purifier series. The quantity and quality of the steam admitted was adjusted by means of valves to meet the required increase in humidity and temperature imposed by the dryness and temperature of the inlet coke oven gas.



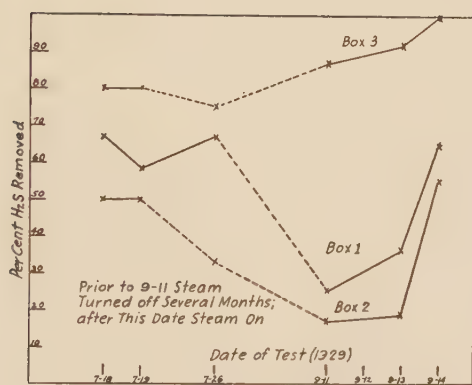
CURVE 12—SERIES I, Box in Position 1.

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CURVE 13—Comparative Efficiencies of Purifiers With and Without Relative Humidity Control. Comparison of Use of Live and Exhaust Steam in Boxes.

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CURVE 14—Efficiencies of Purifiers, Series G.

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This part of the investigation was largely conducted on Series (H) since, as already pointed out, it was one of the more inefficient series in the plant. However, some data were also obtained on the comparatively efficient Series (G). The results of these tests are shown in Curves 13 and 14.

TABLE VIII
THE EFFECT OF HUMIDITY AND TEMPERATURE CONTROL

Box	Date	Test No.	Per Cent Efficiency Without Control			Per Cent Efficiency With Control			Average Increase in Eff. With Control		
			1	2	3	1	2	3	1	2	3
7-17-29	1		7	71	50						
7-18	2		3	52	43						
7-19	3		21	37	25						
7-25	4		19	53	50						
7-31	5*		42	90	99	42	90	100			
8-1	6*		42	89	100	42	89	100			
8-2	7		14	58	80						
9-6	8		16	57	69						
9-7	9					35	92	100			
9-8	10					33	89	100			
9-9	11					42	87	100			
9-10	12					50	93	100			
9-11	13					43	93	100			
9-12	14*	46	92	100		46	92	100			
9-13	15	9	53	81							
9-14	16	35	82	100							
Box Average		23	67	73		42	91	100	19	24	27
Series Average									23.3		

In the case of the inefficient series (H) the average increase in efficiency resulting from the application of humidity and temperature control was determined to be 23%. This value was found by comparing the results obtained by control with the results obtained without close control. In the tests made without close control an attempt was made to follow as closely as possible the usual plant practice.

In this usual plant method when a series showed a stain on the outlet gas of the last or fourth purifier box with the steam off, the steam was turned on, and allowed to remain on until the series again showed a stain on the outlet, when the steam was again shut off. This cycle was repeated as nearly as possible several times in these tests. Determinations of the efficiency of hydrogen sulphide removal were made at representative points in the series of tests simulating this usual practice, and also in the series of tests under the more closely controlled conditions.

The two methods of operation may best be compared by reference to Curve 13, on which are plotted the results of these tests. The calculation of the 23.3% average increase in efficiency obtained with humidity and temperature regulation is shown in Table VIII.

The effect of humidity on the comparatively efficient series (G) is shown on Curve 14. This illustrates the importance of control. It had

*Note: The data obtained in these tests were credited to the results obtained both with and without control because Test No. 5, for example, was made at the end of the period of testing without control, therefore, it also represents the beginning of the period with control.

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not been necessary to give this series any attention, and the steam to it had been turned off for several months because of the light summer load. The iron oxide had therefore dried out considerably, and consequently its efficiency for the removal of hydrogen sulphide had been reduced. When exhaust steam was turned on, however, it began to show improvement within two days, and continued to improve for the period of the test, which was discontinued because of the lack of time.

RESULTS OF TESTS ON WATER GAS PURIFICATION

In the time available no conclusive data could be obtained on the effect of humidity on water gas purification. The gas was saturated with moisture before it entered the purifiers. Further, it was not possible to remove this moisture, as there was no available means for drying the gas. It was not possible, therefore, to obtain various humidities for investigation. It is believed, however, that when this type of gas contains over 0.4% oxygen the effect of humidity will be similar to that on coal gas. This will be further discussed below.

DISCUSSION OF RESULTS—ECONOMIC SIGNIFICANCE

The data presented in Curve 13 and Table VIII show conclusively that an important increase in the power of an old and badly fouled box to remove hydrogen sulphide may be obtained by maintaining the proper temperature and humidity control. The efficiency of such a box was approximately doubled, thus greatly lightening the load on the succeeding boxes. The improvement in the operation of boxes 2 and 3 was likewise very pronounced and important. If the above tests with and without control are typical, and every endeavor was taken to make them so, humidity and temperature control should permit a marked reduction in the cost of removing hydrogen sulphide from gas. Opponents of this conclusion may point out that no important decrease need be expected because (1) a major portion of the cost of the purification consists of capital charges, which will continue because the boxes are installed and must be paid for whether the full capacity is required under improved operating conditions or not; (2) a box in the series must be dumped when the back pressure on the series becomes excessive, and this condition is not controlled by the efficiency of the hydrogen sulphide removal, but by the deposition of tar, oil and naphthalene, and the hardening of the oxide, and this cost is therefore not decreased by the application of the control methods; (3) an important cause of the decrease in the removal power of a box is the coating of the oxide by the deposition of tar and oil, and this is not prevented by humidity and temperature control; (4) an old and badly fouled box is never operated to complete exhaustion, but is changed when, after passing all four boxes of the series, the gas is not and cannot be maintained clean, therefore a large increase in the efficiency of the old box is not of great significance; (5) the use of a high humidity and temperature carries an objectionable amount of water vapor into the holders and ultimately into the distrib-

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uting system; (6) the apparent advantages accruing as a result of humidity control are not real because the determinations were made during the summer months and would not apply during the winter months when the gas load is heavier and the velocity of flow through the boxes greater.

While these arguments against the importance of humidity control seem formidable, it is believed that a careful consideration of each will still lead to the conclusion previously stated, namely, that the constant and effective control of the temperature and relative humidity at optimum predetermined points should lead to a marked reduction in the costs of the purification.

Consider each objection in detail. While it may be true that the increase in capacity does not at once give relief from capital charges, it is, nevertheless, true that manufactured gas plants under normal conditions must meet a constantly increasing demand. Equipment sufficient to meet present-day requirements becomes inadequate in a few years, and additional capital costs must be incurred for additional construction unless some method can be found to increase the capacity and efficiency of the present equipment. If such a method can be found—and the control of the relative humidity appears to be such a method—then to this method should be credited the economy effected when the costs, otherwise necessary for the construction, are saved.

The second point, which concerns the limitations placed upon a system by the pressure conditions, likewise yields to further consideration. A method of operation which will give completely clean gas with three boxes when four were formerly required must reduce pressure troubles due to the reduction in the depth of material through which the gas must travel. If it is not desired or not considered wise to eliminate the fourth box less purifying material can be used in each box in order to reduce the pressure drop. If desired, more shavings can be exposed to the entering tar fog, thereby reducing the material cost.

It is well known that the intermittent soaking and desiccation of a gelatinous and clayey material such as commercial iron-oxide shaving mixtures tends to give lumps and preferred passages. Unquestionably, the texture of the purifying mass will be much more even and open and the pressure drop through it will be much less if this mass is conditioned to a satisfactory predetermined humidity and temperature and then maintained constantly under these conditions. The maintenance of the humidity will prevent the drying out, which leads to much of the hardening. The reduction of tar and oil troubles should be sought in another manner, but it is not amiss to point out in passing that an increase in purifying capacity due to a better method of operation may, under some conditions, release, temporarily at least, boxes for use as shavings scrubbers.

It should also be remembered that a box operating under the higher activity and capacity clearly made possible by the proper humidity and

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temperature control removes considerably more hydrogen sulphide from a given volume of gas. The tar and oil conditions do not become correspondingly worse, however. In consequence, when a box must be dumped because of unsatisfactory pressure conditions due to this cause, the fouled oxide carries out a correspondingly greater quantity of sulphur and has consequently given a lower cost per unit weight of sulphur removed. This general principle is true for boxes dumped for similar causes, as, for example, in anticipation of the winter load.

These considerations also dismiss the third point, concerning the reduction in the life of the oxide due to the coating with tar and oil. Unquestionably an increase in the capacity and efficiency of the oxide process will permit a much greater latitude in handling the tar and oil contamination problem, and permit a lower cost of purification.

Point four as an argument against the necessity for striving for a high removal in the first box is fallacious. Every endeavor should be made to secure the maximum removal of hydrogen sulphide in the old first box, because such a removal lightens the load on the succeeding boxes, thereby insuring for these a longer life.

The possibility that the maintenance of a high humidity at a temperature of 95° F. may throw an objectionable amount of water into the distribution system is worthy of some consideration.

From the purifiers, the gas is usually passed through meters, then in some plants to the naphthalene scrubber and then to the holders, from which it is drawn as needed for the city. In plants equipped with a dehydrating system there is no problem. In all plants the gas loses temperature to the ground, and during very much of the year it loses temperature to all the surroundings. The amount of water carried as a vapor therefore is determined not by the temperature and humidity of the purifiers, but by the resultant lower temperature. The increased humidity upon the purifiers will therefore appear chiefly as entrained moisture. Where inadequate provisions for removing entrained moisture exist, and the holder capacity is inadequate, this entrained moisture is often thrown upon the distribution system.

Fortunately in most plants when the atmospheric temperatures are the highest the holder capacity is generally adequate, permitting the dropping of much of the entrainment by making into one holder and drawing out from another.

Where the conditions are extreme, this research points a humidity relief hitherto not previously disclosed to the knowledge of the writer, at least. Intermittent revivification in place may be practiced, in which case the moisture content of the exit revivifying gases is not of consequence. In the sulphiding the maximum efficiency corresponds to a humidity of about 65%, and this may be maintained, thus dismissing the objection.

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It is therefore believed that this argument against humidity control can be met by engineering measures which are convenient and economical, and that it should not be urged as an objection.

Taking up the other outlined objection, namely, the attack upon the determinations made under summer conditions as non-representative, there is here unfortunately a lack of sufficient information. To answer this scientifically and conclusively would require a systematic and complete study of the particular plant under consideration for a period of at least a year. For the purposes of this dissertation such a study was impossible and unnecessary. It is probable, however, that such a study may show additional data in favor of controlled temperatures and humidities. Usually the gas comes to the box colder during the winter, and the necessary heat is supplied either by direct low or high pressure steam or by indirect heating by means of steam coils. It is obvious that, in those cases where indirect heating is largely relied upon, a very undesirable drying-out may occur, with a pronounced decrease in the efficiency and capacity. An attempt to correct this by the use of open steam may very readily lead to an excessive soaking of the oxide with very unfavorable results. Since in the winter time the demand for gas usually fluctuates more rapidly, as the gas is colder and the volume handled is greater, it would appear that attempts to control the conditions by alternately increasing or decreasing or shutting off the steam to the boxes without systematic humidity control would lead to results varying more sharply and more widely from the desired average, and thus be consequently even more unfavorable than those obtained when this system was employed during the summer. Certainly the writer knows at present no *a priori* reason which dictates the conclusion that the proper humidity and temperature control would be less favorable in the winter than in the summer.

While it is beyond the interest and the purpose of this dissertation to attempt any exact economic evaluation of humidity control; and it is recognized that such an exact evaluation is impossible without a complete and systematic study of each particular plant for a long period of time, nevertheless the writer of this dissertation, in view of the foregoing considerations, maintains the belief that a marked reduction in purification costs should follow the intelligent application of this control, coupled, of course, with temperature control.

SUMMARY

The literature of certain problems relating to the removal of hydrogen sulphide from manufactured gas by means of iron oxide has been reviewed, and the lack of published information concerning the humidity conditions necessary for efficient operation has been noted.

In the laboratory, the humidity conditions, at a certain temperature, have been studied both for the primary sulphiding reaction and the revivifying reaction, which subsequently converts the sulphided material again to the oxide; and the more desirable relative humidities have been ascertained.

In this study, a suitable test for following rapidly, under controlled conditions, the heterogeneous reaction between hydrogen sulphide and iron oxide was needed and has been developed. This test has been described.

The fundamental information developed in the laboratory was applied to the purifying operations of a large gas company. The results confirmed the laboratory conclusions and showed the possibility of obtaining important economies in the cost of the purification.

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BIOGRAPHICAL NOTE



Charles Gordon Milbourne, son of Elijah Broughton and Mary (Ott) Milbourne, was born in Baltimore, Maryland, on September 4, 1902. He attended the grade schools of Baltimore, and was graduated from the Baltimore Polytechnic Institute in February, 1922. He entered the Johns Hopkins University in September, 1922, and received the degree of Bachelor of Science in Chemistry in June, 1925. During his undergraduate residence, he was the holder of a State Scholarship.

Prior to his entering the University, he was employed as Laboratory Assistant in the plant laboratory of the United States Industrial Chemical Company two months, and in the Chemical Laboratory of the Baltimore Tube Company six months. During the summer months of 1923 he was employed in the Drafting Room of the Bethlehem Steel Company, Sparrows Point, Maryland. He was a member of the training course of the Atlantic Refining Company, Philadelphia, Pennsylvania, during the summer of 1924. After receiving his B. S. degree he was employed as a Research Chemist with the E. I. duPont de Nemours and Company at their Experimental Station, Wilmington, Delaware, where he was engaged upon the high pressure catalysis of water gas from June, 1925, until February, 1927.

He entered the Department of Gas Engineering at the Johns Hopkins University as a graduate student in February, 1927, receiving the Rufus C. Dawes Scholarship of the Mobile Gas Company, Mobile, Alabama, during the first year. He returned to the Experimental Station of the duPont Company during the summer of 1927, and was again engaged upon high pressure research. He was Laboratory Assistant in the evening extension course on Gas and Fuel Analysis in the Department of Gas Engineering of this University during 1927-1928. He was Superintendent's Aid at the Spring Gardens plant of the Consolidated Gas Electric Light and Power Company of Baltimore during the summer of 1928. He received scholarship aid from The Koppers Company, Pittsburgh, Pennsylvania (Mr. H. B. Rust, President), during the last two years of graduate work. He is a member of the American Chemical Society and Sigma Xi.

